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THE INSTITUTE OF METALS

MINUTES OF PROCEEDINGS

GENERAL MEETING

16 February 1955

A GENERAL MEETING of the Institute of Metals was held in the University, Edgbaston, Birmingham, at 10.30 a.m. on Wednesday, 16 February 1955. The Chair was taken by Mr. W. J. THOMAS, Chairman of the Metallurgical Engineering Committee.

INFORMAL DISCUSSION ON "THE TREATMENT OF SWARFS, SAWINGS, AND RESIDUES IN THE NON-FERROUS METALS INDUSTRY"

An all-day Informal Discussion took place, to which numerous contributions were made. Dr. E. Scheuer, Dr. F. M. Pinoff, Mr. J. H. Dickin, and Mr. E. D. Burn gave opening addresses. A summarized report of the discussion is published in the *Bulletin*, 1954-55, vol. 2, pp. 275-277.

At the conclusion of the meeting, a vote of thanks was passed to the University authorities for permission to use the Mechanical Engineering Department lecture theatre for the meeting.

ANNUAL SPRING MEETING

29 March to 1 April 1955

THE FORTY-SEVENTH ANNUAL SPRING MEETING of the Institute of Metals was held in London from Tuesday to Friday, 29 March-1 April 1955.

Tuesday, 29 March

MAY LECTURE

The Forty-Fifth Annual May Lecture on "The Nature of the Real Crystal", was delivered by Professor F. C. FRANK, O.B.E., D.Phil., F.R.S., University of Bristol, in the Lecture Theatre of The Royal Institution, Albemarle Street, London, W.1, at 7.0 p.m. The President, Dr. S. F. DOREY, C.B.E., F.R.S., occupied the Chair.

At the conclusion, Professor F. C. THOMPSON, D.Met. (Past-President) proposed a vote of thanks to Professor Frank for his lecture.

Later in the evening, the Council entertained the Lecturer to dinner at the Army and Navy Club, Pall Mall, S.W.1.

Wednesday, 30 March

ANNUAL GENERAL MEETING

THE FORTY-SEVENTH ANNUAL GENERAL MEETING was held at Church House, Great Smith Street, London, S.W.1, at 10.0 a.m. The retiring President, Dr. S. F. DOREY, C.B.E., F.R.S., occupied the Chair at the opening of the meeting.

The minutes of the previous General Meetings, held in London on 25 and 26 November 1954 and in Birmingham on 16 February 1955, were taken as read and signed by the Chairman.

Elections of Members, Junior Members, and Student Members

The Secretary (Lieut.-Colonel S. C. GUILLAN, T.D.) announced that since the General Meeting held in London on 25-26 November 1954, a total of 173 new members had been elected on 31 December 1954, and 25 January, 10 February, 4, 16, and 30 March 1955, the lists of whose names are printed in the *Bulletin*, 1954-55, vol. 2, pp. 214, 220, 231, and 243.

Report of Council for the Year Ended 31 December 1954

The Chairman moved, Mr. A. E. R. WILLIS seconded, and there was carried unanimously, a motion for the adoption of the Report of Council for the year ended 31 December 1954,

which is published on pp. 306-315 of this volume of the *Journal*.

Report of the Honorary Treasurer and Accounts for the Financial Year Ended 30 June 1954

Mr. J. C. COLQUHOUN, M.B.E. (Honorary Treasurer) moved that the Report of his predecessor in office, Mr. E. H. JONES, and the accounts for the financial year ended 30 June 1954 be adopted. The motion was seconded by Mr. G. L. BAILEY, C.B.E., M.Sc. (Vice-President) and carried unanimously.

The Report and accounts are printed in this volume of the *Journal*, pp. 316-320.

Re-Election of Auditors

Mr. T. HENRY TURNER, M.Sc., moved, Mr. RAYMOND LEMMY seconded, and it was carried unanimously that the Institute's auditors, Messrs. Poppleton and Appleby, be re-elected for the year 1955-56.

Election of Officers for 1955-56

The Secretary announced that the following members had been elected to fill vacancies on the Council for the year 1955-56:

President:

MAURICE COOK, D.Sc., Ph.D.

Vice-Presidents:

E. H. JONES

W. J. THOMAS

Honorary Treasurer:

J. C. COLQUHOUN, M.B.E.

Ordinary Members of Council:

L. E. BENSON, D.Sc.

C. F. J. FRANCIS-CARTER, O.B.E.

D. P. C. NEAVE, M.A.

Professor H. O'NEILL, M.Met., D.Sc.

Election of Senior Vice-President for 1955-56

The Secretary announced that the Council had elected Major C. J. P. BALL, D.S.O., M.C., to be Senior Vice-President for 1955-56 and that he would be their nominee for the Presidency in 1956-57.

Vote of Thanks to Retiring Officers

Dr. Ivor JENKINS proposed, and there was carried with acclamation, a vote of thanks to the following retiring officers for their services on the Council: Professor A. J. Murphy, M.Sc., Past-President; Mr. G. L. Bailey, C.B.E., M.Sc., Vice-President, and Mr. K. W. Clarke and Mr. Christopher Smith, Ordinary Members of Council.

Induction of the New President

The Chairman, Dr. S. F. DOREY, C.B.E., F.R.S., then introduced the new President, Dr. MAURICE COOK, inducted him into the Chair, and invested him with the Presidential Badge.

Vote of Thanks to the Retiring President

Dr. L. B. PFEIL, O.B.E., A.R.S.M. (Vice-President), proposed, Mr. S. S. SMITH, M.Met. (Chairman of the Birmingham Local Section), seconded, and there was carried with acclamation a hearty vote of thanks to the retiring President, Dr. S. F. DOREY, C.B.E., F.R.S., for his services to the Institute. Dr. Dorey briefly responded.

Presidential Address

Dr. MAURICE COOK then delivered his Presidential Address, which is printed on pp. 433-443 of this volume of the *Journal*.

A vote of thanks to the President for his Address was proposed by Mr. CHRISTOPHER SMITH, and carried with acclamation.

Institute of Metals (Platinum) Medal

The Secretary announced that the Institute of Metals (Platinum) Medal for 1955 had been awarded to Dr. COLIN JAMES SMITHELLS, M.C., Director of Research, The British Aluminium Co., Ltd., in recognition of his services to metallurgical science, to the metal industries, and to the metallurgical profession. He said that, as Dr. Smithells was then in the United States, the medal would be presented to him at the Autumn Meeting.

Rosenhain Medal

The President presented the Rosenhain Medal for 1955 to Dr. WILLIAM ALBERT BAKER, Research Manager, The British Non-Ferrous Metals Research Association, in recognition of his outstanding contributions to knowledge in the field of physical metallurgy, with special reference to the influence of gases and shrinkage on the soundness of cast metals.

W. H. A. Robertson Medal and Premium

The President presented to Professor HUGH FORD, D.Sc., Ph.D., Wh.Sch., and Mr. J. G. WISTREICH, M.Sc., D.I.C., the W. H. A. Robertson Medal and Premium for 1954, which had been awarded for their paper on "Problems of the Control of Dimension, Shape, and Finish in the Rolling of Sheet and Strip and in the Drawing of Wire", published in the *Journal*, 1953-54, vol. 82, pp. 281-290.

Students' Essay Prizes

The Secretary announced that, as a result of the 1954 Students' Essay Prize Competition, a First Prize had been awarded to Dr. A. P. Miodownik, B.Sc., of Battersea Polytechnic, London, for an essay on "The Significance of Microhardness Testing" (printed in the *Bulletin*, 1954-55, vol. 2, pp. 258-262), and that a Second Prize had been awarded to Mr. SURINDAR SINGH for an essay on "The Kirkendall Effect".

The President presented the first prize to Dr. Miodownik; Mr. Singh was unable to be present.

The Annual General Meeting then concluded.

DISCUSSION OF PAPERS

At the resumed meeting in the afternoon at Church House, Great Smith Street, London, S.W.1, two concurrent scientific sessions were held, as follows:

DISCUSSION ON "REFRACTORIES FOR LOW-FREQUENCY INDUCTION FURNACES"

Under the Chairmanship of Mr. CHRISTOPHER SMITH, a discussion was held based on the following two papers previously published in the *Journal*. The papers were presented by Mr. J. C. HOWARD, B.Met., who acted as Rapporteur:

"The Choice and Construction of Monolithic Linings for Twin-Bath Induction Furnaces for Melting Aluminium Alloys", by E. J. Thackwell.

"The Use of Refractories in Low-Frequency Induction Furnaces for Melting Copper Alloys", by Maurice Cook, D.Sc., Ph.D., F.I.M., C. L. M. Cowley, B.Sc., A.I.M., and E. R. Broadfield, B.Sc.

DISCUSSION ON "FATIGUE"

Under the Chairmanship of Dr. N. P. INGLIS, M.Eng. (Member of Council), a discussion was held based on the following papers published in the *Journal*. Major P. C. VARLEY, M.B.E., T.D., M.A., acted as Rapporteur:

"Some Further Observations on the Fatigue Process in Pure Aluminium", by P. J. E. Forsyth, A.I.M.

"Fatigue Phenomena in High-Strength Aluminium Alloys", by R. F. Hanstock, Ph.D., F.Inst.P.

"The Creep and Fatigue Properties of Some Wrought Complex Aluminium Bronzes", by J. McKeown, D.Sc., F.I.M., D. Mends, B.Sc., A.I.M., E. A. Bale, L.I.M., and A. D. Michael, B.Sc., A.I.M.

"The Influence of Sub-Structure on the Slip Observed in Pure Aluminium and Some Aluminium Alloys When Subjected to Fatigue Stresses", by P. J. E. Forsyth, A.I.M., and C. A. Stubbington.

"The Effect of Internal Oxidation on the Fatigue Properties of Copper Alloys", by J. W. Martin, M.A., Ph.D., and G. C. Smith, M.A.

At the conclusion of each discussion a vote of thanks to the authors and rapporteur was proposed by the Chairman and carried with acclamation.

CONVERSAZIONE

In the evening, a Conversazione was held at the Headquarters of the Institute of Physics, 47 Belgrave Square, London, S.W.1.

Thursday, 31 March

At the resumed meeting at 10.0 a.m. at Church House, Great Smith Street, London, S.W.1, two concurrent scientific and technical sessions were held: (i) an all-day Symposium on "The Control of Quality in the Production of Wrought Non-Ferrous Metals and Alloys. Part III.—The Control of Quality in Heat-Treatment and Final Operations", and (ii) a discussion on the theme "The Constitution of Uranium Alloys".

SYMPOSIUM ON "THE CONTROL OF QUALITY IN THE PRODUCTION OF WROUGHT NON-FERROUS METALS AND ALLOYS. PART III.—THE CONTROL OF QUALITY IN HEAT-TREATMENT AND FINAL OPERATIONS"

At the morning session, the Chair was taken by the President, Dr. MAURICE COOK. Dr. A. R. E. SINGER, as Rapporteur, introduced the following six papers (see this volume of the *Journal*, pp. 193-270).

At the afternoon session, at 2.30 p.m., the Chair was taken by Mr. W. J. THOMAS (Vice-President), Chairman of the Metallurgical Engineering Committee.

There was an all-day discussion, a report of which is printed on pp. 508-528 of this volume of the *Journal*.

"Assessment of Quality of Wrought Products", by W. G. Shilling, M.C., D.Sc., F.Inst.P.

"The Control of Quality in Heat-Treatment and Final Operations in the Production of Rolled, Extruded, and Drawn Aluminium and Aluminium Alloys", by A. J. Field, M.C., B.Sc., F.I.M., and J. Salter, B.Sc.Tech., A.M.I.E.E.

"Heat-Treatment and Finishing Operations in the Production of Copper and Aluminium Rod and Wire", by H. J. Miller, M.Sc., F.I.M.

"The Control of Quality in the Heat-Treatment and Finishing of Copper and Copper-Base Alloys", by V. B. Hysel, M.Sc., A.I.M., and T. W. Collier.

"The Production of Light-Alloy Drop-Forgings, Their Heat-Treatment, Inspection, and Testing", by W. T. Edmunds, B.Sc., and R. C. Lloyd, A.I.M.

"The Heat-Treatment, Inspection, and Testing of Wrought Nickel and Nickel Alloys", by W. Betteridge, Ph.D., F.Inst.P., and T. E. Cound, B.Sc., A.I.M.

At the conclusion of the Symposium a hearty vote of thanks to the authors and to the rapporteur was proposed by the Chairman and carried with acclamation.

DISCUSSION ON "THE CONSTITUTION OF URANIUM ALLOYS"

At the morning session, under the Chairmanship of Professor G. V. RAYNOR, M.A., D.Phil., D.Sc. (Vice-President), a discussion was held based on the following papers which had been published in the *Journal*. The papers were presented by Dr. H. M. FINNISTON, who acted as Rapporteur:

"A Survey of the Uranium-Nickel System", by J. D. Grogan, B.A., and R. J. Pleasance. With an Appendix by (Miss) B. E. Williams on "An X-Ray Examination of Some Uranium-Nickel Alloys".

"The System Uranium-Lead", by B. R. T. Frost, B.Sc., Ph.D., and J. T. Maskrey.

"The System Uranium-Mercury", by B. R. T. Frost, B.Sc., Ph.D.

"The Constitution of Uranium-Zirconium Alloys", by D. Summers-Smith, B.Sc., Ph.D., A.R.T.C.

"Pseudo-Binary Phase Sections Between Laves Phases in Ternary Alloys of Uranium", by G. B. Brook, B.Met., G. I. Williams, B.Sc., Ph.D., and (Mrs.) E. M. Smith, B.A.

DISCUSSION ON "TWINNING"

At an afternoon session, under the Chairmanship of Professor F. C. THOMPSON, D.Met. (Past-President), a discussion took place based on the following papers which had been published in the *Journal*:

"The Formation and Removal of Twins in Titanium During Deformation", by A. T. Churchman, Ph.D., B.Sc., A.I.M.

"Growth Twins in Crystals of Low-Co-ordination Number", by E. Billig, D.Sc.Tech., M.I.E.E.

"Twinning and Untwinning in Polycrystalline Magnesium", by R. L. Woolley, M.A., Ph.D., A.Inst.P.

DISCUSSION ON "DEFORMATION AND FRACTURE OF ZINC"

The afternoon session was continued, under the Chairmanship of Professor F. C. THOMPSON, D.Met. (Past-President), when a discussion was held, based on the following papers previously published in the *Journal*:

"Some Observations on the Deformation of Zinc at High Temperatures", by R. W. Cahn, Ph.D., (Miss) I. J. Bear, A.M.T.C., and R. L. Bell, B.Sc.

"The Cleavage Fracture of Polycrystalline Zinc in Tension", by G. W. Greenwood, B.Sc., Ph.D., and Professor A. G. Quarrell, D.Sc., Ph.D., A.R.C.S.

At the conclusion of each discussion, the Chairman proposed a vote of thanks to the authors and rapporteur, which was carried with acclamation.

DINNER AND DANCE

In the evening, a Dinner and Dance was held at Grosvenor House, Park Lane, London, W.1. The President was in the Chair.

Friday, 1 April

VISITS TO WORKS

Visits were paid to the following works: W. H. A. Robertson and Co., Ltd., Bedford; W. H. Allen and Co., Ltd., Bedford; K. and L. Steelfounders and Engineers, Ltd., Letchworth; Foster Instrument Co., Ltd., Letchworth; Wild-Barfield Electric Furnaces, Ltd., Watford; G. A. Harvey and Co. (London), Ltd., London, S.E.7; Vauxhall Motors, Ltd., Luton.

The meeting then concluded.

ANNUAL AUTUMN MEETING

19 to 23 September 1955

THE FORTY-SEVENTH ANNUAL AUTUMN MEETING of the Institute of Metals was held in Buxton and Sheffield from Monday 19 to Friday 23 September 1955.

Monday, 19 September

The meeting opened at the Palace Hotel, Buxton, at 3 p.m., when two scientific sessions were held simultaneously.

DISCUSSION ON "TRANSFORMATIONS IN COPPER ALLOYS"

Under the Chairmanship of Mr. G. L. BAILEY, C.B.E., M.Sc., a discussion was held based on the following four papers published in the *Journal*; the papers were presented by a rapporteur, Dr. J. W. CHRISTIAN:

"The Bainitic Transformation of the Beta Phase in Copper-Zinc Alloys", by R. D. Garwood, M.Sc.

"Isothermal Transformations of Hypo-Eutectoid Aluminium Bronzes", by R. Haynes, B.Met., Ph.D., A.I.M.

"Isothermal Transformations of Eutectoid Aluminium Bronzes", by R. Haynes, B.Met., Ph.D., A.I.M.

"Some Observations on Isothermal Transformations of Eutectoid Aluminium Bronzes Below Their M_s Temperatures", by R. Haynes, B.Met., Ph.D., A.I.M.

DISCUSSION ON "CORROSION OF ALUMINIUM ALLOYS"

Under the Chairmanship of Dr. A. EDWARDS, B.Sc. (Chairman of the Sheffield Local Section), a discussion was held on the following two papers published in the *Journal*; Mr. E. A. G. LIDDIARD, M.A., acted as Rapporteur:

"Corrosion-Fatigue Properties of an Aluminium-Magnesium-Silicon Alloy in the Unprotected, Anodized, and Painted Conditions", by N. P. Inglis, Ph.D., M.Eng., M.I.Mech.E., F.I.M., and E. C. Larke, A.M.I.Mech.E., A.I.M.

"The Interactions of Static Stress and Corrosion with Aluminium Alloys", by F. A. Champion, B.Sc., Ph.D., A.R.C.S., F.I.M.

DISCUSSION ON "DEFORMATION AND CREEP OF ALUMINIUM ALLOYS"

Under the Chairmanship of Dr. A. EDWARDS a discussion then took place on the following four papers, published in the *Journal*. The papers were presented by Dr. N. P. ALLEN, as rapporteur:

"Some Metallographic Observations of the Creep of Aluminium-Copper Alloys", by A. H. Sully, M.Sc., Ph.D., F.Inst.P., F.I.M., and H. K. Hardy, M.Sc., Ph.D., A.R.S.M., A.I.M.

"Grain-Boundary Movement, Slip, and Fragmentation During Creep of Aluminium-Copper, Aluminium-Magnesium, and Aluminium-Zinc Alloys", by D. McLean, D.Sc., and M. H. Farmer, B.Sc., A.I.M., F.R.M.S.

"Some Observations on the Creep of Pre-Strained Aluminium", by G. R. Wilms, B.Met.E., M.Eng.Sc., Ph.D.

"Plastic Deformation of Aluminium-3.5% Copper Alloy Single Crystals", by K. M. Carlsen, Sivilingeniør, and R. W. K. Honeycombe, M.Sc., Ph.D.

At the conclusion of each discussion a vote of thanks to the authors and rapporteur was proposed by the Chairman and carried with acclamation.

CIVIC RECEPTION

In the evening, a Civic Reception for members and their guests was given at the Palace Hotel, Buxton, by the Mayor and Corporation of Buxton.

Tuesday, 20 September

WELCOME TO VISITORS

The resumed meeting opened at 10.30 a.m. in the Firth Hall, University of Sheffield, in the presence of the Lord Mayor and Lady Mayoress of Sheffield, when the President, Dr. MAURICE COOK took the Chair and welcomed members and delegates attending from overseas.

GENERAL MEETING

The minutes of the Spring Meeting, held in London from 29 March to 1 April 1955, were taken as read and signed by the Chairman.

Elections of Ordinary Members, Junior Members, and Student Members

The Secretary (Lieut.-Colonel S. C. GUILLAN, T.D.) announced that since the last General Meeting a total of 148 new members had been elected on 28 April, 2 and 30 June, 1 and 17 August, and 16 September 1955, lists of whose names are printed in the *Bulletin*, 1954-55, vol. 2, pp. 255 and 268, and 1955-56, vol. 3, pp. 2, 9, and 25.

Election of Officers for 1956-57

The Secretary announced that, as required by the Articles of Association, the following members would retire from the Council at the 1956 Annual General Meeting :

President :

MAURICE COOK, D.Sc., Ph.D.

Past-President :

C. J. SMITHELLS, M.C., D.Sc.

Vice-Presidents :

Major C. J. P. BALL, D.S.O., M.C.

Professor G. V. RAYNOR, M.A., D.Sc., D.Phil.

Ordinary Members of Council :

ALFRED BAER, B.A.

N. I. BOND-WILLIAMS, B.Sc.

N. P. INGLIS, Ph.D., M.Eng.

IVOR JENKINS, D.Sc.

A. G. RAMSAY, Ph.D., B.Sc.

H. SUTTON, C.B.E., D.Sc.

He stated that, in accordance with Article 19, Dr. MAURICE COOK would fill the vacancy as Past-President, and that, in accordance with Article 22, the Council had nominated the following members to fill the other vacancies :

As President :

Major C. J. P. BALL, D.S.O., M.C.

As Vice-Presidents :

N. P. INGLIS, Ph.D., M.Eng.

IVOR JENKINS, D.Sc.

As Ordinary Members of Council :

G. L. BAILEY, C.B.E., M.Sc.

J. W. BERRY

G. E. DONO, J.P.

H. M. FINNISTON, B.Sc., Ph.D.

Professor HUGH FORD, D.Sc., Ph.D., Wh.Sch.

C. H. M. HOLDEN

Senior Vice-President for 1956-57

The SECRETARY announced that, in accordance with Article 42, the Council had elected Dr. L. B. PFELL, O.B.E., A.R.S.M., F.R.S., to serve as Senior Vice-President for 1956-57, and that he would be their nominee for the Presidency in 1957-58.

AUTUMN LECTURE

The Chairman introduced Dr. C. SYKES, F.R.S., who delivered the Twenty-Sixth Autumn Lecture on "The Development and Improvement of Research Techniques". At the conclusion, a vote of thanks to the lecturer was proposed and carried with acclamation. The lecture is printed in the *Journal*, 1955-56, **84**, 287-290.

OFFICIAL LUNCHEON

After the morning meeting, members and guests were entertained at luncheon by the Reception Committee at the Royal Victoria Hotel, Sheffield. Dr. A. EDWARDS, B.Sc. (Chairman of the Sheffield Local Section), was in the Chair.

VISITS

In the afternoon members paid visits to the Research Laboratories of the British Iron and Steel Research Association, Sheffield, and to the works of the Chesterfield Tube Co., Ltd., Chesterfield; Davy and United Engineering Co., Ltd., Sheffield; Edgar Allen and Co., Ltd., Sheffield; Firth-Brown Tools, Ltd., Sheffield; Millspaugh, Ltd., Sheffield; and Walker and Hall, Ltd., Sheffield. Visits were paid by the ladies to Haddon Hall and the works of Batchelors Peas, Ltd., Wadsley Bridge, and Walker and Hall, Ltd., Sheffield.

*Wednesday, 21 September**VISITS*

Members paid all-day visits to the works of Thomas Bolton and Sons, Ltd., Froghall; David Brown Companies, Ltd.,

Penistone; English Steel Corporation, Ltd., Sheffield; Thos. Firth and John Brown, Ltd., and Firth-Vickers, Ltd., Sheffield; and Steel, Peech and Tozer and the Swinden Research Laboratories of The United Steel Companies, Ltd., Rotherham. The ladies visited the factories of the Royal Crown Derby Porcelain Co., Ltd., Derby, or Josiah Wedgwood and Sons, Ltd., Stoke-on-Trent, in the morning, and Chatsworth House and gardens in the afternoon.

Thursday, 22 September

The President, Dr. Maurice Cook, took the Chair at 9.30 a.m.

INSTITUTE OF METALS (PLATINUM) MEDAL FOR 1955

The President presented to Dr. COLIN JAMES SMITHELLS, M.C., the Institute of Metals (Platinum) Medal for 1955, in recognition of his services to metallurgical science, to the metal industries, and to the metallurgical profession. The award had previously been announced at the 1955 Spring Meeting. Dr. Smithells briefly acknowledged the honour bestowed on him by the Institute.

At 9.45 a.m., two scientific sessions were held simultaneously.

DISCUSSION ON "WORKING PROPERTIES OF METALS"

Under the Chairmanship of Dr. L. B. PFELL, O.B.E., F.R.S. (Vice-President), a discussion took place based on the following three papers published in the *Journal*; the papers were presented by a rapporteur, Mr. G. L. BAILEY, C.B.E., M.Sc. :

"The Effect of Strain Rate and Temperature on the Resistance of Aluminium, Copper, and Steel to Compression", by J. F. Alder, M.A., Ph.D., Grad.I.C.E., and V. A. Phillips, A.R.S.M., B.Sc., D.Eng., A.I.M.

"A Hot Impact Tensile Test and Its Relation to Hot-Working Properties", by E. A. Leech, M.Sc., A.I.M., P. Gregory, A.I.M., and R. Eborall, M.A.

"Inhomogeneous Deformation in Rolling and Wire-Drawing", by B. B. Hundy, B.Sc., Ph.D., A.I.M., and A. R. E. Singer, B.Sc., Ph.D.

DISCUSSION ON "RADIATION DAMAGE TO METALS AND ASSOCIATED PROBLEMS"

Under the auspices of the Metal Physics Committee, a discussion was held on "Radiation Damage to Metals and Associated Problems". The Chair was taken by Professor A. G. QUARRELL, D.Sc., Ph.D., A.R.C.S., D.I.C. (Chairman of the Reception Committee). Brief introductory addresses were given by Dr. M. J. Makin, Mr. O. Plail, Dr. P. C. L. Pfeil, Mr. S. F. Pugh, and Dr. J. H. O. Varley (in his absence, Mr. S. F. Pugh's address was presented by Dr. H. M. Finniston).

At the conclusion of each discussion, the Chairmen proposed, and there was carried with acclamation, a vote of thanks to the authors, rapporteur, and opening speakers.

VOTES OF THANKS

At a concluding session, at 12.20 p.m., with the President, Dr. MAURICE COOK, in the Chair, Major C. J. P. BALL, D.S.O., M.C. (Senior Vice-President), moved the following resolution : "That the best thanks of the Institute of Metals be, and are hereby, extended to :

(i) The Chairman and Members of the Sheffield Local Section for their kind invitation to the Institute to hold this Autumn Meeting in Buxton.

(ii) Professor A. G. QUARRELL, D.Sc., Ph.D., A.R.C.S., D.I.C., and the members of the Reception Committee and Executive Committee for the excellent arrangements made for the meeting.

(iii) The companies and individuals who so generously subscribed to the Hospitality Fund in connection with this meeting.

(iv) His Worship the Mayor of Buxton for his welcome and for his hospitality.

(v) The Directors of the following establishments and companies for their invitations to members and guests to visit their works and laboratories and for their hospitality : Edgar

Allen and Co., Ltd.; Batchelors Peas, Ltd.; Thomas Bolton and Sons, Ltd.; The Brightside Foundry and Engineering Co., Ltd.; The British Iron and Steel Research Association; The David Brown Companies, Ltd.; Brown Bayley Steels, Ltd.; The Chesterfield Tube Co., Ltd.; Davy and United Engineering Co., Ltd.; Derbyshire Silica Firebrick Co., Ltd.; English Steel Corporation, Ltd.; H. J. Enthoven and Sons, Ltd.; Firth-Brown Tools, Ltd.; Thomas Firth and John Brown, Ltd.; Firth-Vickers, Ltd.; Hadfields, Ltd.; Mappin and Webb, Ltd.; Millspaugh, Ltd.; Royal Crown Derby Porcelain Co., Ltd.; Sheepbridge Alloy Castings, Ltd.; Solus-Schall, Ltd.; Steel, Peech, and Tozer; Stephenson, Blake and Co., Ltd.; The United Steel Companies, Ltd.; Walker and Hall, Ltd.; Josiah Wedgwood and Sons, Ltd.

(vi) All others who have contributed in any way to the success of this meeting."

Mr. E. A. G. LIDDIARD, M.A., seconded the motion, which was put to the meeting and carried with acclamation.

Dr. A. EDWARDS (Chairman of the Sheffield Local Section) replied on behalf of the Institute's hosts, and referred to the great amount of work carried out in connection with the arrangements for the meeting by Professor A. G. QUARRELL (Chairman of the Reception Committee).

The business meeting then terminated.

VISITS

In the afternoon, members paid visits to the works of The Brightside Foundry and Engineering Co., Ltd., Sheffield; Brown Bayley Steels, Ltd., Sheffield; Derbyshire Silica Firebrick Co., Ltd., Friden; H. J. Enthoven and Sons, Ltd., Darley Dale; Mappin and Webb, Ltd., Sheffield; Sheepbridge Alloy Castings, Ltd., Sutton-in-Ashfield; Solus-Schall, Ltd., Matlock; and Stephenson, Blake and Co., Ltd., Sheffield.

The ladies visited Hardwick Hall and gardens.

BANQUET

In the evening, the Reception Committee entertained members and guests at a banquet at the Palace Hotel, Buxton. The Lord Mayor of Sheffield, Alderman J. CURTIS, presided.

Friday, 23 September

Members and ladies took part in an all-day tour of the Peak District of Derbyshire.

The meeting then terminated.

RECEPTION COMMITTEE

The arrangements for the meeting were made with the assistance and advice of a Reception Committee constituted as follows:

THE LORD MAYOR OF SHEFFIELD (Alderman J. Curtis)

THE MASTER CUTLER (Mr. W. G. Ibberson)

THE PRESIDENT OF THE SHEFFIELD CHAMBER OF COMMERCE (Mr. F. A. Hurst)

Dr. W. E. ALKINS	Mr. HORACE JENKINSON
Mr. E. AYRES	Mr. R. C. JEWELL
Mr. H. BULL	Mr. E. M. H. JOYCE
Dr. H. H. BURTON	Mr. S. S. LEVICK
Mr. E. W. COLBECK	Mr. H. H. MUMBY
Mr. M. F. DOWDING	Mr. A. S. PEARCE
Dr. A. EDWARDS	Mr. J. H. RUSSELL
Dr. E. GREGORY	Mr. F. H. SANITER
Mr. D. HALL	Mr. HARRY SMITH
Mr. G. L. HANCOCK	Dr. C. SYKES
Mr. G. T. HARRIS	Mr. A. TORRY
Mr. H. A. JENKINSON	Mr. J. G. WIDDOWSON

EXECUTIVE COMMITTEE

Professor A. G. QUARRELL (Chairman)

Major F. ORME, T.D. (Honorary Treasurer)

Dr. A. EDWARDS	Mr. A. J. MACDOUGALL
Mr. M. M. HALLETT	Dr. W. R. MADDOCKS

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EXTRAORDINARY GENERAL MEETING

22 September 1955

AN EXTRAORDINARY GENERAL MEETING was held at the Palace Hotel, Buxton, at 9.15 a.m. on Thursday, 22 September 1955. The President, Dr. MAURICE COOK, was in the Chair.

The SECRETARY (Lieut.-Colonel S. C. GUILLAN, T.D.) read the notice convening the meeting.

SPECIAL RESOLUTION

After explaining its purpose, the Chairman moved the following Special Resolution amending the Articles of Association:

THAT the Articles of Association of the Institute be amended in the manner following, that is to say:—

(a) In Article 5 by the deletion of the word "or" and the insertion after the words "Student Members" of the words "or Overseas Sustaining Members".

(b) In Article 6 by the insertion immediately prior to the ultimate paragraph of such Article of the following new paragraphs:

Overseas Sustaining Members shall be such bodies corporate having their headquarters or principal places of business outside the United Kingdom of Great Britain and Northern Ireland and desiring to give financial support to the objects and work of the Institute, as the Council in its absolute discretion shall admit as Overseas Sustaining Members. The decision of the Council on the question of eligibility for admission as an Overseas Sustaining Member shall be final.

An Overseas Sustaining Member shall be entitled to nominate not more than two individuals for membership of the Institute and further individuals from time to time in place of any such nominee not being elected or ceasing to be a nominated Member provided that an individual so nominated must be eligible for election as an Ordinary Member, Junior Member, or Student Member and shall submit a signed application for membership and shall be subject to election by the Council in accordance with these Articles.

An Overseas Sustaining Member shall not be qualified for election to the Council. An Overseas Sustaining Member shall neither be entitled to receive notice of nor to attend nor vote at any General Meeting of the Institute nor to vote upon a ballot. Save as herein otherwise provided, a Member nominated by an Overseas Sustaining Member shall have all the rights and privileges and shall be subject to the conditions appertaining to the class of membership to which he shall be admitted. Save as aforesaid, during any period in which there shall be no individual Member nominated by a particular Overseas Sustaining Member, then such Overseas Sustaining Member shall have all the rights and privileges and shall be subject to the conditions appertaining to an Ordinary Member.

A Member nominated by an Overseas Sustaining Member shall be entitled at any time during membership to elect by notice in writing to the Council as from the date of service of such notice to continue in membership in his own right and in all respects as if he were not a nominated member.

All nominations by an Overseas Sustaining Member and revocations of such nominations shall be made in writing under the hand of an officer duly authorized in that behalf by the Board of Directors or equivalent governing body of such Overseas Sustaining Member.

(c) In Article 8 by the deletion of the word "or" where it first occurs and the insertion after the words "Student Members" of the words "or Overseas Sustaining Members".

(d) In Article 9 by the insertion of the following new paragraph to be numbered 9 (b) and the re-numbering of the existing paragraphs 9 (b), 9 (c), and 9 (d) to read 9 (c), 9 (d), and 9 (e) respectively:

(b) Unless and until otherwise determined by the Council or provided by the bye-laws, each Overseas Sustaining Member shall pay a minimum annual subscription of £25. Such subscription shall be deemed to include the annual subscription of the individual Member or Members nominated by such Overseas Sustaining Member.

(c) In Article 15 by the insertion of the following new paragraph to be lettered (f):

(f) If, in the case of a Member nominated by an Overseas Sustaining Member, such Overseas Sustaining Member shall give to the Council and to the nominated Member not less than fourteen days' notice in writing revoking such nomination or if the Overseas Sustaining Member shall cease to be a Member of the Institute.

(f) In Article 55 by the insertion of the following words at the commencement of the Article:

"Subject as hereinbefore provided as to Overseas Sustaining Members".

Major C. J. P. BALL, D.S.O., M.C. (Senior Vice-President) seconded the motion, which was put to the meeting and carried by the members without dissent.

GENERAL MEETINGS

8 November 1955

A GENERAL MEETING of the Institute of Metals was held at The Royal Institution, Albemarle Street, London, W.1, on Tuesday, 8 November 1955, at 8.30 p.m. The Chair was taken by the President, Dr. MAURICE COOK.

The President introduced Professor CYRIL S. SMITH, Sc.D., Director of the Institute for the Study of Metals, Chicago, who delivered a lecture on "The Shape of Grains in Single-Phase and Two-Phase Alloys", after which there was a discussion.

A vote of thanks to the Lecturer was proposed by Dr. RONALD KING and carried with acclamation.

9 November 1955

A GENERAL MEETING of the Institute of Metals took place at The Royal Institution, Albemarle Street, London, W.1, on Wednesday, 9 November 1955, at 10 a.m. At the opening of the meeting, the Chair was occupied by the President, Dr. MAURICE COOK, who welcomed members and visitors from overseas.

The minutes of the previous General Meetings, held on 19-23 September 1955, in Buxton and Sheffield, and in London on 8 November 1955, were taken as read and signed by the Chairman.

SYMPOSIUM ON "THE MECHANISM OF PHASE TRANSFORMATIONS IN METALS"

The President briefly explained the Council's objects in arranging the Symposium, after which he vacated the Chair, which was taken at the morning session by Professor G. V. RAYNOR, M.A., D.Phil., D.Sc., Vice-President and Chairman of the Metal Physics Committee.

The Chairman called upon Dr. H. K. HARDY, A.R.S.M., who, as rapporteur, presented the following eight papers, after which there was a discussion on "Transformations of the Nucleation-and-Growth Type":

"Nucleation-and-Growth Processes in Metals and Alloys", by H. K. Hardy, D.Sc., Ph.D., A.R.S.M., A.I.M., and T. J. Heal, M.Sc., F.Inst.P.

"Effects of Nucleation Site upon Precipitate Morphology", by H. I. Aaronson, Ph.D.

"The Precipitation of the θ' Phase in Aluminium-4% Copper Alloys", by G. Thomas, B.Sc., and J. Nutting, M.A., B.Sc., Ph.D.

"A Resistometric Study of the Kinetics of Precipitation in Lead-Tin Alloys", by Professor G. Borelius, Fil.Dr., and L. E. Larsson.

"Superlattice Formation in the Alloy CdMg_3 ", by H. Steeple, Ph.D., B.Sc., and Professor H. Lipson, D.Sc., M.A.

"The $\beta \rightarrow \alpha$ Transformation in Pure Tin and its Dilute Alloys", by E. O. Hall, M.Sc., Ph.D., A.Inst.P.

"The Structure of the ω Precipitate in Titanium-16% Vanadium Alloy", by (Miss) J. M. Silcock, B.Sc., M. H. Davies, B.Sc., and H. K. Hardy, D.Sc., Ph.D., A.R.S.M., A.I.M.

"Sigma-Phase Nucleation and Other Transformations During Diffusion in the Iron-Chromium System", by H. J. Goldschmidt, D.Sc., F.Inst.P.

At the afternoon session, the Chair was taken by Professor A. G. QUARRELL, D.Sc., Ph.D., D.I.C.

The Chairman called on Dr. R. W. CAHN, B.A., who, as rapporteur, presented the following ten papers, after which there was a discussion on "Martensitic Transformations".

"Martensitic Transformations", by B. A. Bilby, B.A., Ph.D., and J. W. Christian, M.A., D.Phil.

"The Nucleation Problem in Martensite", by M. A. Jaswon, M.A., Ph.D.

"Homogeneous *versus* Heterogeneous Nucleation in the Martensitic Transformation", by Larry Kaufman, Sc.D., B.Met.E., and Professor Morris Cohen, Sc.D.

"Crystal Geometry of the Austenite-Martensite Transformation", by T. Ll. Richards, B.Sc., Ph.D., F.I.M., and W. T. Roberts, M.Sc., Ph.D.

"The Allotropic Transformation of Cobalt", by François Sebilliau and Hervé Bibring.

"The Diffusionless Transformations of Metastable β -Brass", by D. Hull, B.Sc., and R. D. Garwood, M.Sc.

"The Crystallography of the $\beta \rightarrow \alpha$ Phase Transformation in Uranium-1.4 Atomic Per Cent. Chromium Alloy", by B. R. Butcher, B.Sc., and A. H. Rowe.

"The $\beta \rightarrow \alpha$ Transformation in Uranium-1.4 Atomic Per Cent. Chromium Alloy", by W. M. Lomer, M.Sc., Ph.D.

"The Bainite Reaction in High-Carbon Steels", by Dr. O. Krisement and Professor Dr. F. Wever.

"The Stabilization of Austenite", by S. G. Glover, B.Sc., and T. B. Smith, B.Sc.

At the conclusion of the meeting, the Chairman proposed votes of thanks to the authors and rapporteurs, and also to the Managers of The Royal Institution for permitting the use of their Lecture Theatre for the meeting, which were carried with acclamation.

The papers (Serial Nos. 1630-1647) will be published, together with a report of the discussion, as *Monograph and Report Series No. 18*.

7 December 1955

A GENERAL MEETING of the Institute of Metals was held at 4 Grosvenor Gardens, London, S.W.1, on Wednesday, 7 December 1955, at 6.30 p.m. The Chair was taken by Professor F. C. FRANK, O.B.E., F.R.S.

The minutes of the previous General Meeting, held in London on 9 November 1955, were taken as read and signed by the Chairman.

REPORT ON A RECENT LOW-TEMPERATURE CONFERENCE HELD IN PARIS

The Chairman explained that the object of the Metal Physics Committee in arranging the meeting was to bring to the attention of metallurgists aspects of a recent low-temperature conference held in Paris that related to metals.

After an introduction by Professor Sir FRANCIS SIMON, C.B.E., F.R.S., Professor of Thermodynamics, The Clarendon Laboratory, Oxford, explaining why low temperatures were becoming of increasing importance to the metallurgist, Dr. P. L. SMITH and Dr. H. M. ROSENBERG, of The Clarendon Laboratory, reviewed some of the work presented at the Paris conference on thermal and electrical conductivity, the specific heats of metals, and some mechanical properties at low temperatures. There was then a discussion.

At the conclusion of the meeting, the Chairman proposed, and there was carried with acclamation, a vote of thanks to Sir Francis Simon and his colleagues for their addresses.

GRAIN-BOUNDARY MOVEMENT, SLIP, AND FRAGMENTATION DURING CREEP OF ALUMINIUM-COPPER, ALUMINIUM-MAGNESIUM, AND ALUMINIUM-ZINC ALLOYS *

1558

By D. McLEAN,† D.Sc., MEMBER, and M. H. FARMER,† B.Sc.,
A.I.M., F.R.M.S., MEMBER

(Communication from the National Physical Laboratory.)

SYNOPSIS

Three polycrystalline aluminium alloys (aluminium-copper, aluminium-magnesium, and aluminium-zinc) have been tested in creep, and observations have been made of the movements at grain boundaries, of slip, and of the fragmentation of the original crystals into sub-crystals. It is concluded that slip and grain-boundary displacement take place concurrently and bear a constant ratio to one another during a given test. The magnitude of this ratio depends on the conditions of the test.

I.—INTRODUCTION AND MAIN CONCLUSIONS

ALTHOUGH much study has recently been devoted to the mechanism of creep in "pure" polycrystalline metal, less attention has been given to alloys. It seemed logical, therefore, to follow up the work on aluminium,¹⁻¹⁷ some of which has been summarized by Rotherham,¹⁸ by similar work on pure binary aluminium alloys. It was desired to obtain information about the deformation mechanism in some solid-solution alloys, creep elongation/time curves on which had already been determined;^{19,20} the compositions of the alloys for the present investigation were therefore chosen to lie within the ranges covered in the earlier work. In order to establish quantitative information about the deformation processes occurring during creep, suitable techniques were employed to measure grain-boundary and slip movements and the disorientation between the sub-crystals formed by the breakdown of the original crystals.

The chief conclusions reached were as follows:

(i) Grain-boundary displacements increased with time in a manner very similar to the total extension, a constant relation between the two existing right from the onset of creep. Thus, a plot of grain-boundary displacement against extension was in all cases fitted fairly closely by a straight line, the slope of which depended on the applied stress and the alloying addition. For all specimens in which fragmentation was sufficiently marked for the sub-crystal diameter to be measured, the slope of this line was found to be approximately equal to the diameter of the sub-crystals (the slope having the dimensions of length).

(ii) For all three alloys the fraction of the total extension calculated to be contributed by grain-

boundary movements increased as the applied stress decreased, being about $\frac{1}{15}$ at $\frac{3}{4}$ ton/in.² and about $\frac{1}{2}$ at $\frac{1}{2}$ ton/in.². According to this result, more than half the specimen extension was in most cases due to deformation of the crystals. But the slip bands, unlike those seen in aluminium under the same conditions, were few and small. This apparent discrepancy was resolved by indirect evidence showing that the crystals deformed by a normal slip process to about the required extent. It is therefore concluded that slip was distributed over many more planes in the alloys than in aluminium.

Apart from this difference the main conclusions are similar to those reached with aluminium. There was, however, another small variation in the overall behaviour. Although the aluminium-copper and aluminium-magnesium alloys crept more slowly and the aluminium-zinc alloy faster than aluminium, all three were more stress-sensitive than the pure metal, in the sense that the percentage change in creep rate for a given change in stress was greater.

II.—EXPERIMENTAL DETAILS

The three alloys, the compositions of which are given in Table I, were cast in the form of $2 \times 2 \times 12$ -in. ingots, which were rolled with intermediate annealing to strip $\frac{1}{4}$ in. thick.

In the case of the aluminium-magnesium and aluminium-zinc alloys these compositions are well within the solid-solubility limits (3 and 12 wt.-%, respectively) at 200° C., the temperature at which all the creep tests were made, but the composition of the aluminium-copper alloy is on the borderline for precipitation. Micro-examination of this alloy at room

* Manuscript received 9 October 1953.

† Metallurgy Division, National Physical Laboratory, Teddington, Middx.

temperature showed numerous fine particles of precipitate, the presence of which would in any event be expected on account of the fall in solubility with temperature. Evidence was later encountered (Section III, 2) that most of these particles did not dissolve before or during the creep test, so that the alloy was just within the two-phase region at the temperature of test.

The testing procedure has been described in detail elsewhere.¹³ Briefly, four or five specimens of each alloy were machined from the $\frac{1}{4}$ -in. strip. The specimens were about 6 in. long \times $\frac{1}{4}$ in. thick and tapered in width from 1 to $\frac{3}{8}$ in., so that when a suitable load was applied they covered the range of stress from $\frac{1}{3}$ to $\frac{3}{4}$ ton/in.², or $\frac{1}{4}$ to $\frac{1}{2}$ ton/in.² in the case of three specimens extended for relatively long periods of time.

specimen width at accurately spaced intervals. After testing, the spacing was remeasured, giving, by reason of the taper, curves of elongation against initial stress* (e.g. Fig. 1 (a)). From these, curves of creep elongation against time for particular stresses (e.g. $\frac{1}{2}$ ton/in.², Fig. 2) were obtained by interpolation. The grain-boundary displacements were also measured after extension, and corresponding curves were determined. Fifty measurements were made to obtain each mean value on account of the wide variability from boundary to boundary. Although the actual measurement was of the vertical component of displacement, the values plotted are of total displacement, derived from the former by a simple averaging procedure.¹³

At the end of the test the specimens were sectioned

TABLE I.—*Data on Specimens and Test Conditions.*

Material	Alloy Content *		Annealing Temp., °C.	Grains/mm.	Duration of Creep Test, hr.			
					No. 1	No. 2	No. 3	No. 4
	At.-%	Wt.-%			Stress Range: $\frac{1}{4}$ – $\frac{1}{2}$ ton/in. ²			$\frac{1}{2}$ – $\frac{3}{4}$ ton/in. ²
Al-Cu	0.196	0.46	420	3.37	25	125	550 $\frac{1}{2}$	651 $\frac{1}{2}$, 1816, 3182 $\frac{1}{2}$
Al-Mg	0.21	0.20	400	3.63	25	124	769 $\frac{1}{4}$	1818, 3184 $\frac{1}{2}$
Al-Zn	2.1	4.9	400	3.97	5 $\frac{1}{2}$	25	48 $\frac{1}{2}$	167

* The principal impurities found in the three alloys were Fe 0.002, Si 0.003, Cu (not deliberately added) 0.003 wt.-%.

TABLE II.—*Elongations Produced by Stresses of $\frac{3}{4}$ and $\frac{1}{2}$ Ton/In.².*

Material	Al-Cu			Al-Mg			Al-Zn			Aluminium			
Duration of Creep Test, hr. . .	25	125	550 $\frac{1}{2}$	25	124	769 $\frac{1}{4}$	5 $\frac{1}{2}$	25	48 $\frac{1}{2}$	1	5	25	118 $\frac{1}{2}$
(a) E% at $\frac{3}{4}$ ton/in. ²	2.3	8.8	24	1.73	3.8	15.2	8.9	29	42	3.1	8.4	15.0	29.5
(b) E% at $\frac{1}{2}$	0.025	0.06	0.11	0.01	0.06	0.33	0.45	1.08	1.22	0.33	0.64	0.92	1.30
(a)/(b)	92	147	218	173	63	46	20	27	34 $\frac{1}{2}$	9	13	16	23

The durations of the tests are given in Table I. The specimens were annealed at temperatures chosen to give similar grain-sizes in the three alloys; these temperatures and the resultant grain-sizes, as measured by the linear-intercept method, are also included in Table I. After annealing, all the specimens were furnace-cooled to 200° C. from the annealing temperature, in order to approach the equilibrium condition pertaining to 200° C. and were air-cooled from 200° C. to room temperature. They were then electropolished to produce a surface free from mechanical work. On these surfaces measurements of grain-boundary displacements and slip displacements were made with a Linnik interference microscope, and surface deformations were observed. After insertion in the creep machine, the specimens were held at temperature for about a day before loading.

Before creep testing, lines were scribed across the

transversely at positions where the initial stress had been $\frac{1}{4}$, $\frac{1}{3}$, $\frac{1}{2}$, or $\frac{3}{4}$ ton/in.². These transverse sections were used for polarized-light and X-ray examination.

III.—EXPERIMENTAL RESULTS

1. OVERALL EXTENSION

The curves of elongation against stress for the aluminium-magnesium alloy are given in Fig. 1 (a), and for comparison those taken from previous work on pure aluminium¹³ are given in Fig. 1 (b). As previously stated, over the range investigated all three alloys proved to be more stress-sensitive than the pure metal in the sense that a given alteration in stress produced a proportionately larger change in elongation. The stress-sensitivity decreased in the order Al-Cu, Al-Mg, Al-Zn, aluminium. The elonga-

* The tests were carried out at constant load, so that the stress increased during the test owing to reduction of section.

tions produced by stresses of $\frac{3}{4}$ and $\frac{1}{2}$ ton/in.², and their ratios, are given in Table II.

The alteration in stress-sensitivity due to the small additions of copper and of magnesium was thus quite large, the change brought about by zinc being considerably smaller.

weakening influence. An interesting point which emerged from a comparison of curves for different stresses was that the relative strengths of Al-Cu and Al-Mg alloys were reversed as the stress increased from $\frac{1}{2}$ to $\frac{3}{4}$ ton/in.², the Al-Cu alloy being stronger at low stress but weaker at high stress. This alloy

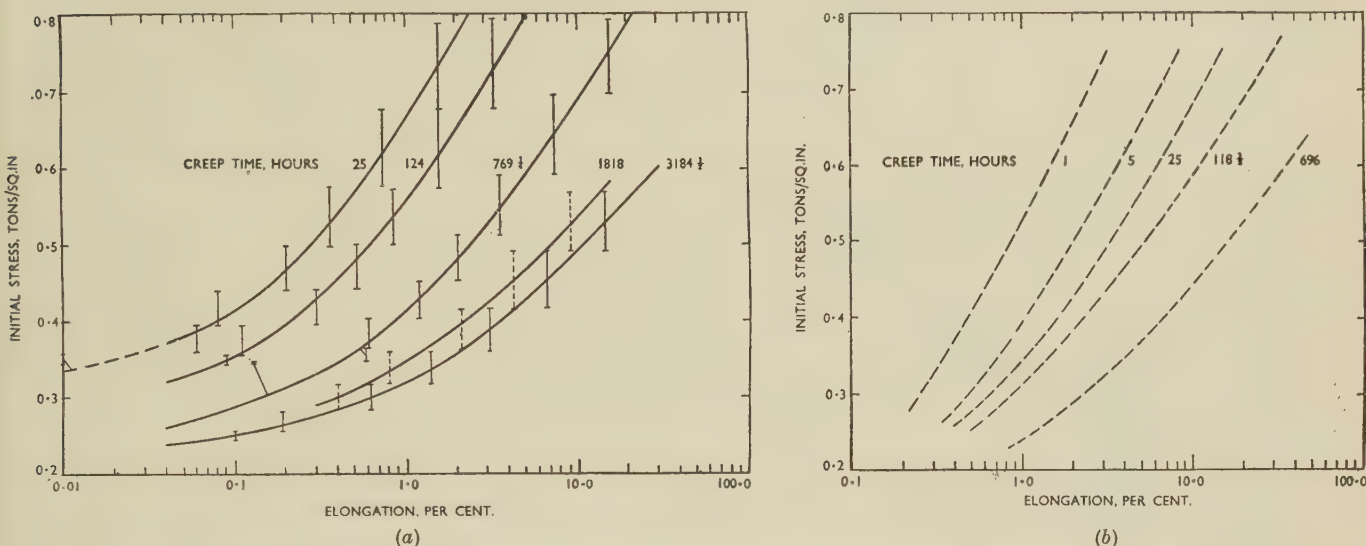


FIG. 1.—Curves of Elongation Against Stress (a) for the Aluminium-Magnesium Alloy, and (b) for Pure Aluminium.

The derived curves of elongation against time for the three alloys are given in Fig. 2, for a stress of $\frac{1}{2}$ ton/in.². That for aluminium is included for comparison.

also becomes relatively stronger with increase of time, and in keeping with this its (a)/(b) ratio in Table II rises with duration of creep, while that for the magnesium alloy falls.

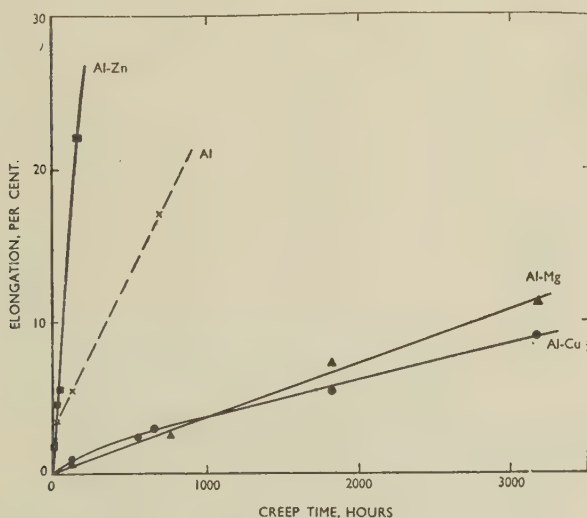


FIG. 2.—Curves of Elongation Against Time for an Initial Stress of $\frac{1}{2}$ Ton/In.².

It is immediately obvious that, whereas copper and magnesium exercise a strengthening effect, zinc has a

2. GRAIN-BOUNDARY MOVEMENTS

The curves of mean grain-boundary displacement (\bar{p}) in microns, plotted against stress, are given in Figs. 3 (a)–(d) for the three alloys and for aluminium, respectively, the latter being taken from previous work.¹⁵ By interpolation, curves of displacement against time were obtained for stresses of $\frac{1}{3}$, $\frac{1}{2}$, and $\frac{3}{4}$ ton/in.². Fig. 4 (which again includes pure aluminium¹⁵) shows the curves for $\frac{1}{2}$ ton/in.². As can be seen by comparing Figs. 4 and 2, for $\frac{1}{2}$ ton/in.², these curves and their interrelations are very similar to the corresponding ones for elongation.

In previous work on aluminium it had been found that a plot of grain-boundary displacement against elongation* for a given initial stress yielded a straight line. Similar plots for the three alloys are given in Figs. 5 (a)–(c). With the exception referred to immediately below, they are all reasonably well fitted by straight lines; the slope of these lines is steeper the lower the stress, in accordance with the fact that relatively more grain-boundary movement would then

* The plot was not against total elongation, but against total elongation minus the elongation due to grain-boundary movement. The latter elongation was calculated from the grain-boundary movement and the number of grain boundaries

and, since all deformation processes, other than the grain-boundary movement, must occur within the crystals, the value plotted, assuming the calculation to be correct, should be equal to the elongation contributed by crystal deformation.

be taking place. The exception concerns the Al-Zn specimen at $\frac{1}{2}$ ton/in.² (Fig. 5 (c)), where the point for specimen No. 4 ($\bar{p} = 7$ microns) lies off the straight line best fitting the other points. The probable reason is that this specimen necked at the position (the narrow end of the taper) where the initial stress was

proportion varies rather more rapidly with stress in the alloys than in pure aluminium. It follows from this that the effect of the alloying additions in raising the stress-sensitivity (Table II, p. 2) operated more strongly as regards the crystal deformation than as regards the grain-boundary deformation.

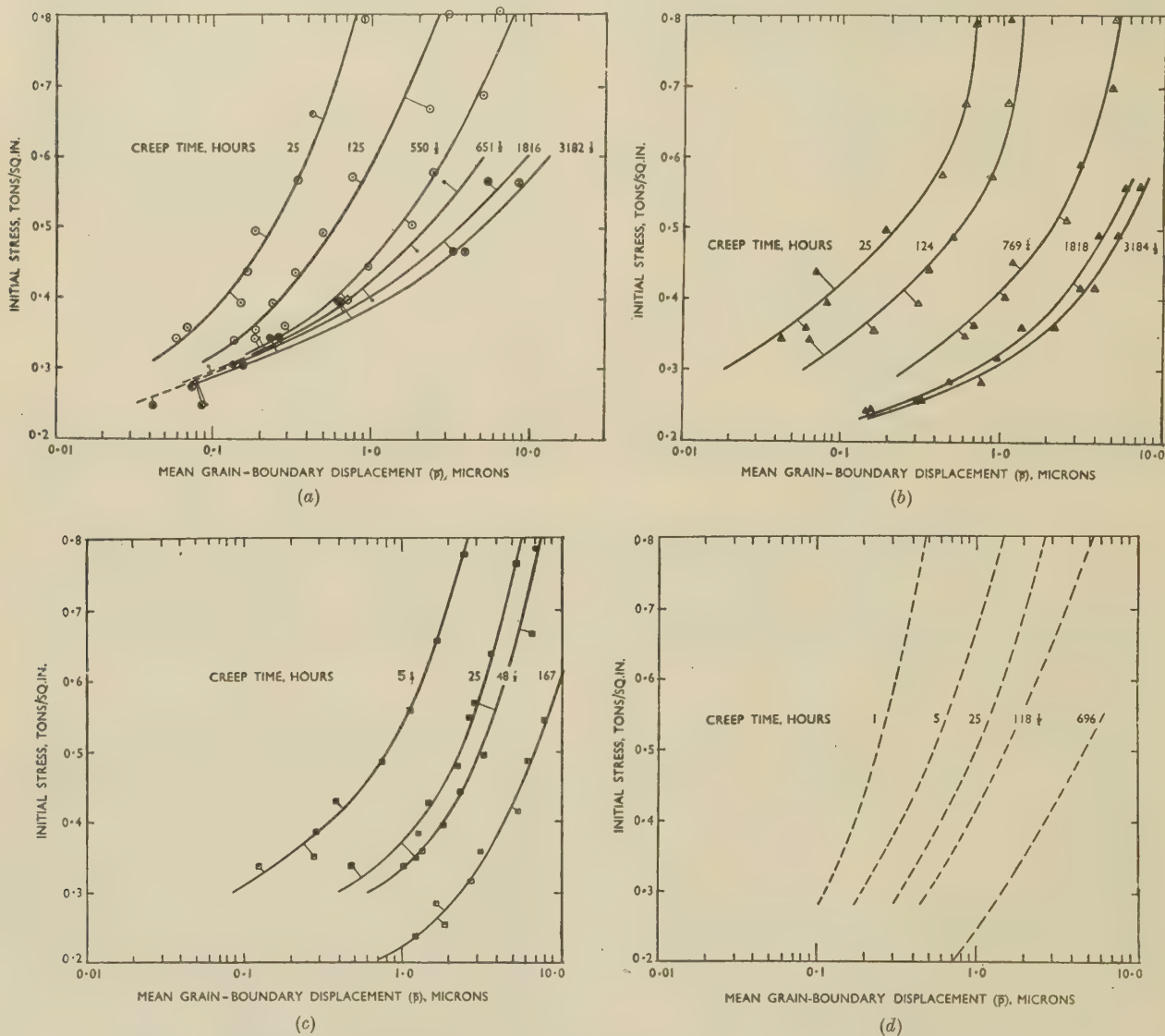


FIG. 3.—Curves of Mean Grain-Boundary Displacement (\bar{p}) Against Stress. (a) Aluminium-copper alloy; (b) aluminium-magnesium alloy; (c) aluminium-zinc alloy; (d) pure aluminium.

$\frac{1}{2}$ ton/in.². This point is further discussed in Section III, 3.

The elongation calculated in this manner as being due to grain-boundary movement, expressed as a fraction of the total elongation, is plotted against stress in Fig. 6. The relationship is very similar for the four materials, the proportion of deformation due to grain-boundary slip increasing with stress to approximately the same extent in each case. There are, however, minor differences, one being that the

During micro-examination of specimen surfaces after deformation, it was noticed in the aluminium-copper specimens that grain boundaries which had undergone displacement often exhibited outlines much more serrated than boundaries in the other alloys or in aluminium. An example is shown in Fig. 7 (Plate I). The serrations were on too fine a scale to be confused with the irregularities connected with breakdown of the main crystals into a sub-crystal structure (see Section III, 3) and resembled more

closely serrations observed on deformed surfaces of pure aluminium.^{5, 9, 10, 11} A possible cause may be the presence of precipitate particles in the aluminium-copper alloy, boundary migration being held up locally by an interfacial attraction to the particles. That the precipitate particles existed at the creep temperature was shown by micro-examination of the originally polished surfaces. In the as-polished, lightly etched condition of the specimen before test, only faint particles of precipitate were to be seen, but after test numerous particles were clearly visible without further etching, presumably the result of oxidation during the creep test. At some boundaries the particles of precipitate were larger than usual, and most

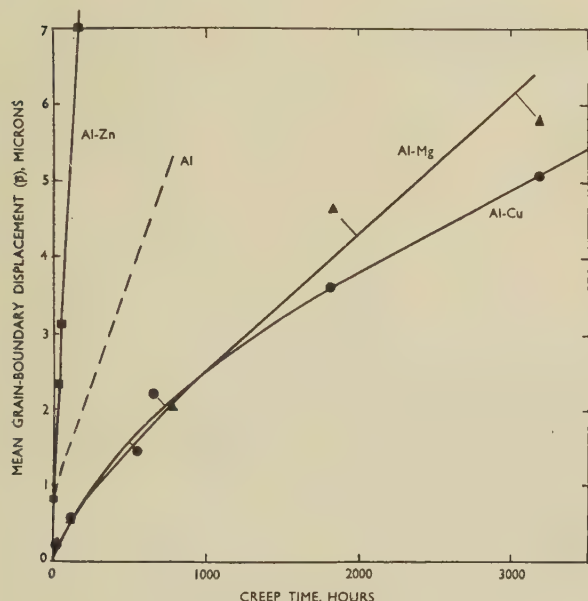


FIG. 4.—Curves of Mean Grain-Boundary Displacement (\bar{p}) Against Time for an Initial Stress of $\frac{1}{2}$ Ton/In.².

of these appeared to be anchored to the crystal on one side, boundary slip being confined to the other. Forsyth²¹ has reported that precipitation may be confined to the surface, in which case the surface does not truly represent the interior. Micro-examination of sections showed that in the present aluminium-copper specimens precipitation was general throughout the interior, and along a few boundaries relatively large particles were seen. Such boundaries, however, seemed less frequent on the sections than on the surface, so that the surface appearance may have exaggerated the true situation.

3. CRYSTAL SLIP AND FRAGMENTATION

On the surfaces of the alloy specimens after deformation there was less sign of slip and sub-crystal formation than on pure aluminium specimens extended by the same amount.^{13, 14} This was the case whether the extension was effected in the same time (Al-Cu and Al-Mg requiring a higher stress than

aluminium; cf. Figs. 8 and 9 (Plate I)); or by the same stress (Al-Zn requiring a shorter time than aluminium; cf. Figs. 10 and 11 (Plate I)). The difference in appearance was more marked in the Al-Cu and Al-Mg alloys than in the Al-Zn alloy, as may be seen from the photographs. These qualitative observations were supported by calculation of the proportion of extension due to visible slip bands (from the number of and displacement at slip bands visible at moderate magnification) in the Al-Cu and Al-Mg specimens on the one hand and in an aluminium specimen extended by a similar amount in a similar time on the other hand. In the former only about $\frac{1}{100}$ of the total extension was due to visible slip bands, whereas in the latter the proportion was about $\frac{1}{10}$. The relative absence of slip bands in the alloys is reasonably interpreted as being attributable to restraint exerted by the solute atoms on the movement of dislocations. That the sub-microstructure affects the appearance of slip bands has also been observed by Edeleanu²² and by Dewhirst (see Brown²³).

Despite the relative absence of visible slip, there was nevertheless indirect evidence that crystal deformation occurred by a normal slip process. The original crystals were observed to break down into sub-crystals, as Wilms and Wood¹ found for aluminium. If the dislocation theory of this breakdown be accepted, there must have been some slip, since according to this theory slip takes place before fragmentation occurs. The theory yields the approximate relation:¹²

$$\text{Percentage elongation associated with the breakdown and due to slip} \approx 100 \times \frac{\text{mean disorientation between neighbouring sub-crystals } (\theta)}{\theta} \quad (1)$$

the disorientation being measured in radians. The elongation due to slip can therefore be derived from measurements of θ , and can be compared with the measured extension. Since the extension calculated from equation (1) relates to deformation within the grains, the left-hand side of the equation relates to the measured total elongation less the extension due to grain-boundary slip, which has been calculated in the course of the preceding section. Relation (1) has been found to hold for aluminium with a scatter of $\sim 2:1$,¹⁴ which is about the magnitude of experimental error in measuring the disorientation θ .

Measurements of the disorientation between neighbouring sub-crystals were made using the polarized-light-anodic-film technique on transverse sections of those alloy specimens which had undergone enough extension for them to contain sub-crystals sufficiently distinct for measurement to be possible. As the measurements were made on transverse sections they are representative of the volume of the specimens, not merely of the surface. The results are given in Table III.

Relation (1) holds equally as well as for aluminium. Unfortunately, the disorientation could be measured only on the few specimens for which results are given in Table III, since the superficial birefringent films

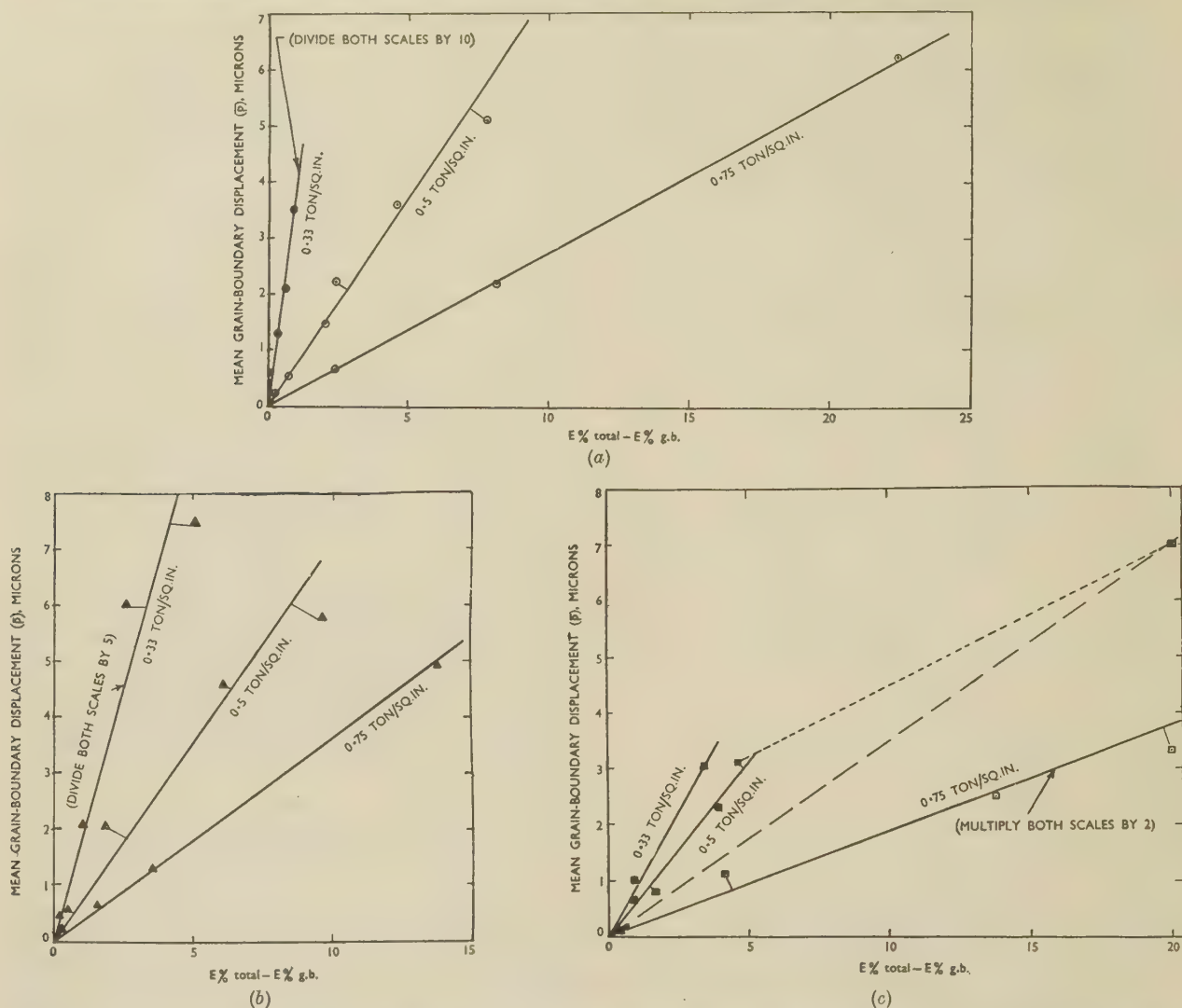


FIG. 5.—Plots of Mean Grain-Boundary Displacement Against Elongation Due to Crystal Deformation (= Total Measured Elongation — Elongation Calculated as Being Due to Grain-Boundary Movement). (a) Aluminium-copper alloy; (b) aluminium-magnesium alloy; (c) aluminium-zinc alloy.

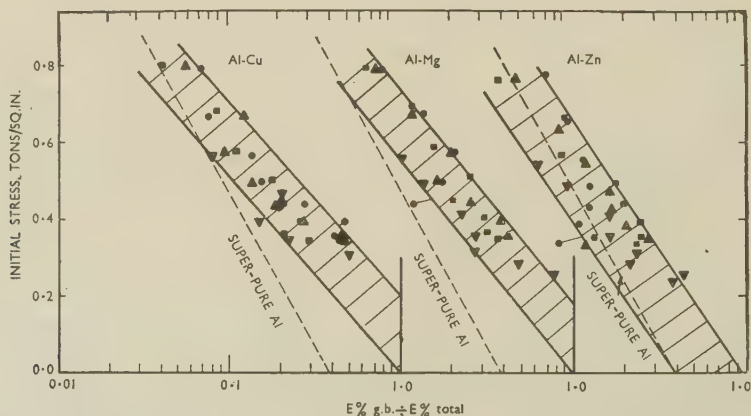


FIG. 6.—Relation Between Stress and Fraction of Extension Due to Grain-Boundary Displacement.



on which the polarized-light method depends were not as perfect with some of the alloys as with aluminium.

It was, however, possible to extend the check on the connection between disorientation and extension by an X-ray method, which proved as suitable experimentally for the alloys as for aluminium and

TABLE III.—*Relation between Extension and Sub-Crystal Disorientation.*

Each value for disorientation θ is the mean of 100 separate measurements.

	Al-Cu	Al-Mg		Al-Zn			
Specimen No. .	No measurements possible	4	4	4	4	3	4
Load, tons/in. ² .		$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{2}{3}$
Disorientation θ , radians .		0.084	0.096	0.035	0.126	0.174	0.309
Extension Calculated from θ ,* %		8.4	9.6	3.5	12.6	17.4	30.9
Measured Extension,† % .		9.6	13.8	3.3	20.1	27.5	40

* From equation (1).

† Total extension less extension calculated from grain-boundary slip.

was applied to the same transverse sections as were used for the polarized-light observations. Extension here again refers to the total extension less that due to grain-boundary slip. Back-reflection X-ray patterns from specimens that have broken down into sub-crystals show arcs in place of the original isolated spots,^{1,6} the arcs being continuous or consisting of discrete spots according to whether the sub-crystals are numerous or few, strained or unstrained. The angle covered by the arcs will obviously be some function of the disorientation between neighbouring sub-crystals. In considering the probable form of this relation it may be recalled that equation (1) is based on the idea that the initially flat lattice planes corrugate sharply during creep, the angle of corrugation being θ . If θ were everywhere equal (i.e. at all corrugations), the initial single X-ray spot would break up into two spots θ apart. In practice, the individual values of θ vary, and an initial single spot therefore breaks up into an arc which covers an angular range depending on the magnitudes both of θ and of the scatter among the individual values of θ . If the reasonable assumption is made that the scatter increases as the mean value increases (though not necessarily linearly), then an approximate relation similar to equation (1) should hold between extension and the mean angle covered by an arc on the X-ray pattern. To make the relation as nearly as possible similar to equation (1), instead of taking the mean angle covered by the arc on the X-ray film, it is better to use the more fundamental quantity, namely the angular range covered by the normals of the reflecting sub-crystals, referred to as α , since this is more nearly comparable to θ ; α can be calculated from the arc by simple geometry.

X-ray back-reflection patterns were accordingly

obtained from all the transverse sections, using filtered CoK_{α} radiation from a sealed-off tube operating at 40 kV. and 14 m.amp. The specimen-film distance was 8 cm. The exposures lasted approximately 2 hr. but were so adjusted that an equal amount of power was consumed during each; this adjustment compensates to a considerable extent for mains variations. The photographic development procedure was kept constant. On each pattern so obtained the total angular distance covered by all arcs was measured and divided by the number of separate arcs to obtain a mean value for one arc. As the number of arcs on each film was limited and the variation in angle covered by them considerable, some scatter from the true mean is to be expected when only one film is used to obtain each mean value, as in the present work. This procedure for obtaining a mean value involves the assumption that arcs from separate crystals do not overlap. As can be seen from Figs. 12 and 13 (Plate II), which are representative X-ray patterns, overlapping would normally not occur except at large extension, when, in fact, complete rings were eventually obtained; patterns giving complete rings were discarded and the corresponding sections were excluded in compiling Table IV. As described above, the angular range α covered by the normals of the reflecting sub-crystals, was calculated from the mean arc. In Table IV α is compared with the extension due to crystal deformation, i.e. ($E\%$ total — $E\%$ g.b.), the ratio of the two being given in the rows "Ratio (A)/(B)" and "Mean Ratio"; values for pure aluminium are also included.

The mean ratios of extension divided by angular range are close to unity for the three alloys and for aluminium, and therefore support the argument outlined above. There is appreciable scatter among individual values, as anticipated, and the ratio tends to decrease at low extension. At least part of this decrease is due to the finite size of the X-ray spots, which sets a lower limit to α , however small the elongation.

Thus, both the polarized-light and the X-ray method indicate that sub-crystal formation is similarly connected with extension in aluminium and the alloys by a relation that can be derived from the dislocation theory of sub-crystal formation. If the dislocation theory is accepted, this fact affords evidence that a large part of the deformation was due to slip. To account for the relative absence of slip markings on the deformed surface of the alloys, it must be assumed either that slip did not reach the surface (Brown²³) or that it took place by very small displacements on very numerous planes, at least as far as the surface was concerned.

Neither the accuracy of the results nor of the derivation of equation (1) is sufficiently good to determine whether all the crystal deformation was due to slip, to the virtual exclusion of any other process. However, the following reasoning, makes this conclusion seem possible. If, under the conditions investi-

gated, two or more processes contributed to the crystal deformation, e.g. if a diffusion process^{24, 25, 26} (as distinct from the diffusion of dislocations which according to the polygonization theory must occur during fragmentation, since any elongation due to that process must be a practically constant fraction of that due to slip) took place, as well as a slip process, it seems likely that the relative amounts contributed by them would vary rather widely over the range of creep rates now covered (25,000:1), as the two processes would be likely to obey different laws. In that event, relation (1) would hold in some cases but not in others. As, in fact, it appears to be generally applicable and to exhibit no consistent trend with change in creep rate

to the sub-crystal diameters in Table V, larger sub-crystals giving larger spots.

The X-ray patterns were examined to see also what qualitative differences they showed between the alloys and pure aluminium. These differences were not large, and were a little obscured by the occasional failure of successive photographs to fall into a regular sequence, presumably owing to inhomogeneity of deformation in the specimen. However, the following two conclusions are based on an examination of over forty X-ray patterns and are thought to be correct statements of the general trend. First, for a given total extension produced in a given time, the Al-Cu and Al-Mg specimens gave more diffuse re-

TABLE IV.—*Relation between Extension and Sub-Crystal Disorientation α Determined from X-Ray Patterns.*

Alloy	Al-Cu						Al-Mg						
Load, tons/in. ²	$\frac{1}{2}$			$\frac{2}{3}$			$\frac{1}{2}$	$\frac{1}{3}$			$\frac{2}{3}$		
Creep time, hr.	125	550 $\frac{1}{2}$	3182 $\frac{1}{2}$	25	125	550 $\frac{1}{2}$	3184 $\frac{1}{2}$	124	769 $\frac{1}{2}$	3184 $\frac{1}{2}$	25	124	769 $\frac{1}{2}$
(A) (E% total — E% g.b.)/100 .	0.008	0.020	0.078	0.0214	0.0815	0.22	0.010	0.005	0.185	0.096	0.016	0.035	0.138
(B) α , radians	0.014	0.018	0.08	0.059	0.069	0.14	0.012	0.011	0.024	0.059	0.023	0.041	0.076
Ratio (A)/(B)	0.57	1.10	0.97	0.36	1.18	1.57	0.83	0.46	0.79	1.63	0.70	0.85	1.82
Mean ratio	0.96						1.01						

Alloy	Al-Zn						Pure Aluminium										
Load, tons/in. ²	$\frac{1}{2}$		$\frac{1}{3}$		$\frac{2}{3}$		$\frac{1}{2}$				$\frac{1}{3}$			$\frac{2}{3}$			
Creep time, hr.	25	48 $\frac{1}{2}$	25	48 $\frac{1}{2}$	5	25	48 $\frac{1}{2}$	5	25	118 $\frac{1}{2}$	696	5	25	118 $\frac{1}{2}$	1	5	25
(A) (E% total — E% g.b.)/100 .	0.009	0.009	0.039	0.046	0.082	0.275	0.40	0.0056	0.0078	0.011	0.030	0.0193	0.031	0.049	0.0193	0.080	0.143
(B) α , radians	0.015	0.037	0.031	0.045	0.020	0.17	0.20	0.014	0.019	0.021	0.017	0.039	0.035	0.044	0.031	0.076	0.133
Ratio (A)/(B)	0.60	0.24	1.26	1.02	4.01*	1.62	2.0	0.40	0.41	0.52	1.77	0.49	0.89	1.11	0.62	1.05	1.08
Mean ratio	1.12 †						0.83										

† Omitting the ratio marked *.

or other conditions, it would seem that over the range involved only one process contributed to crystal deformation. Since some slip undoubtedly occurred, especially in the super-pure aluminium, and since equation (1) is satisfied within the probably error, this one process must have been the normal slip process. It may be noted that Nabarro,²⁵ in examining the micro-creep of tin, concluded that slip was more probably responsible for deformation than was the diffusion of ions.

Visual inspection of the X-ray patterns showed that with increasing extension the sequence of changes was the same in the alloys as in pure aluminium, at the three initial stresses of $\frac{1}{2}$, $\frac{1}{3}$, and $\frac{2}{3}$ ton/in.². In all cases the initially sharp spots first became diffuse and then broke up into small spots that became sharper as extension progressed, as well as spreading further along the Debye circle. This is the sequence of changes observed by Wood and Scrutton.³ By the time the small spots became sharp, secondary-stage creep at constant rate was under way. The sizes of the diffraction spots in the various cases corresponded

flections than aluminium or Al-Zn. The former specimens, of course, required a higher stress. This observation agrees with that of Greenough and Smith,⁶ who found that impure aluminium gave more diffuse spots than a purer aluminium when extended the same amount in the same time, the former requiring a higher stress. Secondly, when a comparison at the same stress was made, it was found that the reflections from Al-Cu and Al-Mg specimens began to sharpen at a lower extension, although after a longer time, than those from pure aluminium or Al-Zn, cf. Figs. 12 and 13 (Plate II) showing patterns from Al-Cu and aluminium, respectively, and Figs 14 and 15 (Plate II) for Al-Mg and aluminium. In both pairs the alloy pattern contains the sharper spots.

The diameters of the sub-crystals were measured on the transverse section, where possible, and, as with aluminium,¹⁵ were found to be closely equal to the slopes of the \bar{p}/E curves (Fig. 5, p. 6). The comparison is given in Table V.

The three sets of figures given for Al-Zn at $\frac{1}{2}$ ton/

in.² help to explain the anomaly in Fig. 5 (c) referred to on p. 4, i.e. that for specimen No. 4 the point ($\bar{p} = 7$ microns) lies off the line best fitting the other points relating to $\frac{1}{2}$ ton/in.². It will be seen from Table V that at this stress the sub-crystal size after necking began (y) was smaller than for the same load

TABLE V.—Comparison of Sub-Crystal Diameter d and \bar{p}/E from Fig. 5 (p. 6).

In each case, d is the mean value for about 500 sub-crystals.

Alloy	Initial Stress, ton/in. ²	(A) \bar{d} , cm. $\times 10^{-3}$	(B) \bar{p}/E , cm. $\times 10^{-3}$	Ratio (A)/(B)
Al-Cu	$\frac{1}{2}$ $\frac{1}{3}$ $\frac{1}{4}$...	37.5	...
		...	7.45	...
		3.00	2.75	1.09
Al-Mg	$\frac{1}{2}$ $\frac{1}{3}$ $\frac{1}{4}$...	17.5	...
		6.61	7.2	0.92
		3.56	3.65	0.98
Al-Zn	$\frac{1}{2}$ $\frac{1}{3}$ $\frac{1}{4}$	8.99	8.8	1.04
		7.81 (w)	6.2 (x)	1.26
		2.43	1.88	1.29
	$\frac{1}{2}$ $\frac{1}{4}$	4.14 (y)	3.50 (z)	1.18
		3.31 †	2.50 †	1.33

* Determined on specimens No. 4, except for (w), which was determined on specimen No. 3, i.e. before necking began.

(x) Relates to the solid line in Fig. 5 (c), covering the period before necking.

(y) and (z) are values after necking; (z) relates to the dashed line in Fig. 5 (c).

† The figures in the bottom row are those corresponding to (y) and (z) for a duplicate specimen.

before necking began (w). A similar result had previously been found¹² in aluminium, and seems a reasonable consequence of the faster rate of deformation that accompanies necking. Table V shows that (comparing values y and z) the \bar{p}/E ratio for specimen No. 4 at $\frac{1}{2}$ ton/in.² is approximately equal to the smaller sub-crystal size. This near equality was confirmed in a duplicate test (see bottom row of table). The duplicate specimen stretched rather more quickly than specimen No. 4, and consequently was removed from test somewhat sooner (after 144½ hr., at which time it had extended a little more than specimen No. 4). The parallel change in sub-crystal diameter and the \bar{p}/E ratio during necking shows that the connection between them is a close one.

Dislocation densities were calculated from the equation:

$$\text{density/cm.}^2 = 2\theta/db$$

where b is the slip distance, for those instances where both θ and d could be measured. The densities were between 10^8 and 10^9 dislocations/cm.².

IV.—DISCUSSION

The creep processes found in pure aluminium, i.e. slip, grain-boundary movement, and sub-crystal formation, seem to occur also in its binary alloys with

copper, magnesium, and zinc. In particular, in spite of the slower rates of deformation employed in the present investigation, which in some cases approached those tolerated in engineering practice, there is evidence that the deformation of the crystals proceeded by a normal slip process and not to any appreciable extent by, for example, a non-crystalline quasi-viscous movement. The linear relationship between grain-boundary movement and crystal deformation found in aluminium was again observed.

In earlier work^{19, 20} on the effect of solutes on the creep elongation/time behaviour of aluminium, it had been found that with limiting contents of 0.32 at.-% copper, 3.25 at.-% magnesium, and 3.94 at.-% zinc, additions of the two former elements steadily increased the creep-resistance, while additions of zinc decreased it, until the solubility limit was approached. The alteration in resistance proceeded smoothly without sudden alterations, suggesting that no sharp changes in mechanism of deformation occurred as the solute content was increased. This suggests that the conclusions set out above apply also to the complete range of alloy contents studied in the present investigation.

During low-temperature deformation the only deformation process considered to occur to any appreciable extent is the dislocation slip process, when the resistance to deformation must be determined by the resistance to slip, i.e. to the movement of dislocations, which becomes greater as deformation proceeds. During secondary-stage creep a metal can continue to deform at constant stress, which implies that the creep rate is controlled by some other process, argued to be a recovery process.^{24, 27, 28} This view presents a means of reconciling the facts that, as compared with aluminium, the aluminium-zinc alloy exhibited a faster creep rate but showed less visible slip, the latter signifying that the zinc solute atoms exerted their normal restraining influence on slip.²⁹ If, despite this restraining influence, the alloy crept faster than the pure metal, some process other than slip must have determined the creep rate. The question then arises where the controlling factor lies, whether in one or other of the two processes observed or in the interaction between the two. While it seems impossible at the moment to answer this question dogmatically, it is worth noting that if the explanation lay in the grain-boundary movement, two difficult problems would automatically be resolved. First, the grain-boundary movement could be small and itself contribute little directly to extension, while nevertheless controlling the main contribution from crystal deformation. This would reconcile the view that grain-boundary movement is often of considerable importance during secondary creep,^{4, 30, 31} with the apparently contradictory theory that much grain-boundary movement cannot occur without considerable crystal deformation. Secondly, such a controlling influence demands some relation between grain-boundary movement and crystal deformation; the linear relation observed in the present work meets

this demand, and thereby becomes the more understandable.

The establishment of this linear relation, and the somewhat similar results obtained by Chang and Grant,¹⁰ throw doubt upon interpretations such as that of Andrade and Jolliffe,³² who consider that primary creep (their β creep) is due to deformation within the grains, and secondary creep (their κ creep) to movement at grain boundaries. If this were so in the case of aluminium or the aluminium alloys now

examined, much less grain-boundary displacement than has been observed would occur during primary creep, and much more during secondary creep.

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REFERENCES

1. G. R. Wilms and W. A. Wood, *J. Inst. Metals*, 1948-49, **75**, 693.
2. W. A. Wood and W. A. Rachinger, *ibid.*, 1949-50, **76**, 237.
3. W. A. Wood and R. F. Scrutton, *ibid.*, 1950, **77**, 423.
4. W. A. Wood, G. R. Wilms, and W. A. Rachinger, *ibid.*, 1951, **79**, 159.
5. G. Wyon and C. Crussard, *Rev. Mét.*, 1951, **48**, 121.
6. G. B. Greenough and E. M. Smith, *J. Inst. Metals*, 1950, **77**, 435.
7. G. B. Greenough, C. M. Bateman, and E. M. Smith, *ibid.*, 1951-52, **80**, 545.
8. I. S. Servi and N. J. Grant, *Trans. Amer. Inst. Min. Met. Eng.*, 1951, **191**, 917.
9. H. C. Chang and N. J. Grant, *ibid.*, 1952, **194**, 619.
10. H. C. Chang and N. J. Grant, *ibid.*, 1953, **197**, 1175.
11. H. C. Chang and N. J. Grant, *ibid.*, 1953, **197**, 305.
12. D. McLean, *J. Inst. Metals*, 1951-52, **80**, 507.
13. D. McLean, *ibid.*, 1952-53, **81**, 133.
14. D. McLean, *ibid.*, 1952-53, **81**, 287.
15. D. McLean, *ibid.*, 1952-53, **81**, 293.
16. W. A. Rachinger, *ibid.*, 1951-52, **80**, 415.
17. W. A. Rachinger, *ibid.*, 1952-53, **81**, 33.
18. L. Rotherham, "Creep of Metals". 1951: London (Institute of Physics).
19. O. D. Sherby, R. A. Anderson, and J. E. Dorn, *Trans. Amer. Inst. Min. Met. Eng.*, 1951, **191**, 643.
20. D. McLean, R. W. Ridley, and A. E. L. Tate, unpublished work.
21. P. J. E. Forsyth, *Bull. Inst. Metals*, 1953, **1**, 150.
22. C. Edeleanu, *J. Inst. Metals*, 1951-52, **80**, 187.
23. A. F. Brown, *Advances in Physics*, 1952, **1**, 427.
24. E. Orowan, *J. West Scotland Iron Steel Inst.*, 1946-47, **54**, 45.
25. F. R. N. Nabarro, *Phys. Soc.: Rep. Conf. on Strength of Solids*, 1948, 75.
26. C. Herring, "The Physics of Powder Metallurgy", edited by W. E. Kingston, p. 143. 1951: London and New York (McGraw-Hill).
27. R. W. Bailey, *J. Inst. Metals*, 1926, **35**, 27.
28. A. H. Cottrell and V. Aytekin, *ibid.*, 1950, **77**, 389.
29. N. F. Mott and F. R. N. Nabarro, *Phys. Soc.: Conf. on Strength of Solids*, 1948, 1.
30. A. H. Sully, "Metallic Creep and Creep-Resistant Alloys". 1949: London (Butterworths Scientific Publications).
31. E. N. da C. Andrade, *Phys. Soc.: Conf. on Strength of Solids*, 1948, 20.
32. E. N. da C. Andrade and K. H. Jolliffe, *Proc. Roy. Soc.*, 1952, [A], **213**, 3.

FATIGUE PHENOMENA IN HIGH-STRENGTH ALUMINIUM ALLOYS*

1559

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SYNOPSIS

The increase in damping capacity that precedes fatigue failure of the aluminium alloys L65 and D.T.D. 683 is associated with precipitate instability. In the alloy D.T.D. 683 localized bands of precipitation have been found, and these are regions where fatigue cracks eventually form.

The localized effects of cyclic stressing do not seriously impair the static strength, but the fatigue strength depends on the magnitude of the stress required to initiate precipitation and on the strength of the over-precipitated regions.

An alloy that derives its high static strength from a controlled state of precipitation that is unstable under cyclic stressing will have a high ratio of static ultimate strength to fatigue strength.

I.—INTRODUCTION

THE static strength of commercial precipitation-hardening aluminium alloys has been raised progressively over a period of years, but this improvement has not been accompanied by a proportional increase in fatigue strength. Roughly, an increase in ultimate strength from 25 to 35 tons/in.² is associated with only about 10% improvement in fatigue strength.

The observations of pre-fatigue phenomena in two high-strength alloys to be described suggest a reason for this discrepancy.

II.—EXPERIMENTAL METHOD

The specimen is subjected to alternating torsional stresses of such a magnitude that fatigue failure eventually occurs. During the fatigue test the damping capacity, $\Delta E/E$, is measured continuously to detect changes occurring in the hysteresis loss expressed as a fraction of the maximum strain energy,

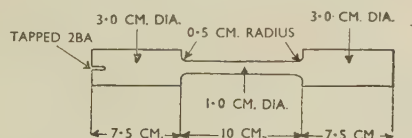


FIG. 1.—Dimensions of the Specimen Used for Damping/Strain Measurements.

E , of the vibrating specimen. This fraction is an expression of the shape of the hysteresis loop, the area of which is the irrecoverable work/cycle, ΔE .

The experimental technique has been described before.¹ In brief, the specimen, having the form shown in Fig. 1, is hung vertically by a fine steel wire. The ends are of large diameter and act as inertias which, rotating in opposite directions, impose shear strain upon the central section of smaller diameter.

This shear strain is uniform at the surface, but decreases linearly with the radius on passing from the periphery to the centre of the circular cross-section of the strained region.

A specimen of suitable dimensions has a natural torsional frequency of about 1000 cycles/sec. This vibration frequency is excited by inducing a current loop in one of the ends of the specimen by surrounding it with a pair of coils connected in series and tuned to the power output of a valve amplifier. A magnetic field is so disposed that its reaction with the induced current applies an alternating torque to the end of the specimen. At the resonance frequency the other end of the specimen vibrates sympathetically with a phase difference of 180° and, because of the low damping of the system, a large vibration amplitude is developed with a moderate power supply (up to 350 W.).

The surface strain in the central section is calculated from an optical measurement of the amplitude of the end sections. Aluminium alloys are essentially elastic under the stresses imposed and the surface strain may be taken as a measure of the surface stress. A vibration detection device similar to that used for excitation is placed at the opposite end of the specimen to supply a frequency signal to the valve amplifier. The complete system is thus an electro-mechanical oscillator operating at the resonant frequency of the specimen, the amplitude of which is controlled by the gain of the valve amplifier. To a good approximation, the total damping of the system is directly proportional to the ratio of the excitation current, I , and the detector voltage, V .

For many aluminium alloys the damping is low ($<10^{-4}$) and independent of stress until quite high stresses are reached, so that it is possible to determine a proportionality factor between the damping determined from the logarithmic decrement and the ratio $I:V$ in the range where the damping is independent of the stress. At higher stresses, where the logarithmic

* Manuscript received 12 January 1954.

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mic decrement cannot be determined easily, the actual damping may be inferred from the corresponding ratio $I:V$.

The form of specimen, mode of stressing, and method of suspension are chosen on the basis of earlier investigations¹ to provide a mechanical system having very low damping (about 2×10^{-5}) attributable to sources other than the internal damping of the material under investigation. In some cases specimens have been examined microscopically after vibration, employing standard techniques for sectioning and polishing, and where necessary etching with aqueous 25% nitric acid.

III.—COMPOSITION AND TREATMENT OF THE ALLOYS

Specimens were machined from heat-treated extruded bar of $1\frac{1}{4}$ in. dia., with the following nominal compositions:

	Cu	Mg	Si	Mn	Zn, %
L65 *	4.4	0.6	0.7	0.6	...
D.T.D. 683 †	0.4	2.7	...	0.5	5.3

* Hiduminium 66.

† Hiduminium RR77.

The L65 alloy was solution-treated at 500°–505° C. for 2 hr., quenched in water at 20° C., and aged for 6 hr. at 185° C. The D.T.D. 683 alloy was solution-treated at 460° C. for 4 hr., quenched in water at 20° C., and aged for 8 hr. at 135° C.

IV.—PRE-FATIGUE VARIATION OF THE DAMPING OF ALLOY L65

The variation of the damping of alloy L65 during fatigue tests is shown in Fig. 2, and Table I gives further information relating to the specimens examined. The initial damping (column 4) is that first measured after about 10^5 cycles, during which the fatigue strain was established. The damping at a much lower strain (1×10^{-4}) was approximately

TABLE I.—*Torsion Fatigue of Alloy L65.*

Specimen No. (see Fig. 2)	Measured Surface Shear Strain, $\times 10^4$	Calculated Surface Shear Stress, tons/in. ²	Initial Damping, $\times 10^5$	Stress Cycles Applied, $\times 10^{-4}$	Final Condition of Specimen
1	48.2	9.09	87	1.5	Cracked
2	45.0	8.49	33	9.2	Not cracked
3	42.5	8.02	27	14.3	Cracked
4	40.0	7.55	20	26.5	"
5	37.5	7.07	16	52.4	Not cracked
6	35.0	6.60	14	141	Cracked
7	32.5	6.13	12	214	"

10×10^{-5} for all specimens. This value includes the unavoidable external damping. Thus on raising the strain from 10^{-4} to 32.5×10^{-4} (Specimen No. 7) the damping increases by only 2×10^{-5} , though further small increments of alternating strain cause progressively larger increases in damping.

The most interesting feature of Fig. 2 is the rise in damping that follows continuous operation of alternating strain. At high strains (Curve 1) the increase is evident from the beginning of the fatigue test, but at strains towards the lower end of the fatigue range there is a quiescent stage during which the damping increases almost imperceptibly during many millions

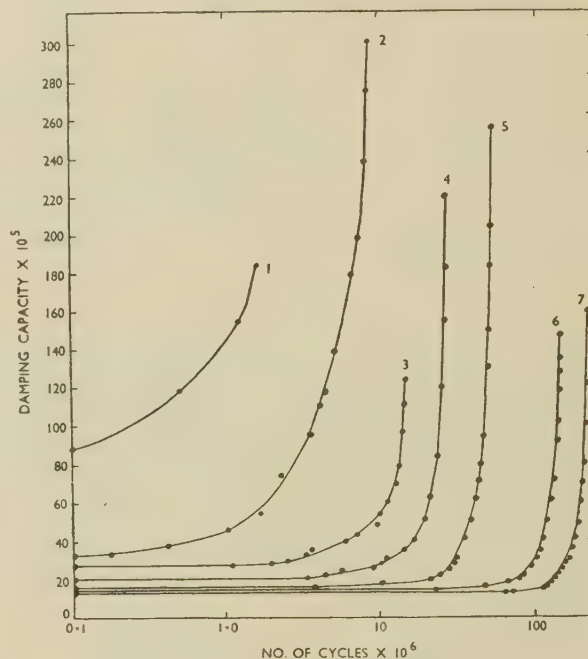


FIG. 2.—Changes in Damping of L65 During Vibration at Constant Strain.

KEY.

- | | |
|-------------------------------------|-------------------------------------|
| 1. Strain = 48.2×10^{-4} . | 5. Strain = 37.5×10^{-4} . |
| 2. Strain = 45.0×10^{-4} . | 6. Strain = 35.0×10^{-4} . |
| 3. Strain = 42.5×10^{-4} . | 7. Strain = 32.5×10^{-4} . |
| 4. Strain = 40.0×10^{-4} . | |

of cycles. The tests on Specimens No. 1, 3, 4, 6, and 7 ended with the formation of large fatigue cracks, but the preceding rise in damping cannot be attributed to the growth of the cracks, for none was found in Specimens No. 2 and 5, although they had final damping capacities higher than the other specimens. The damping increases still further during the formation and growth of a crack to large dimensions, but this increase, although observed for Specimens 1, 3, 4, 6, and 7, is not shown in Fig. 2 because the selected fatigue strains could not be maintained once a large crack had formed.

V.—INSTABILITY OF ALLOY L65 UNDER ALTERNATING STRAIN WITHIN THE FATIGUE RANGE

The increase of damping shown in Fig. 2 may indicate that alternating strains above a certain magnitude cause changes in the state of the alloy. Previous experience shows that such changes cannot be detected with certainty by tensile and hardness

tests on specimens that have been subjected to alternating strains. However, it is also known that the variation of damping with strain is characteristic of the state of an alloy, provided that the number of strain alternations to which the material is subjected during the test are insufficient to disturb its state significantly. This characteristic dependence of damping on strain has been used to investigate the difference between L65 in the conditions of initial low and final high damping shown in Fig. 2.

In the series of observations summarized in Fig. 3, the change induced in L65 by alternating strain is correlated with changes brought about by heat-treatment. All the observations were made on one

The curves in Fig. 3 (h)–(l) show the variation of damping with strain after heating the specimen at 400°, 425°, 450°, 475°, and 500° C., respectively, followed by quenching and ageing. These curves show the approach to, and final attainment of, the original condition represented by Fig. 3 (a), which is regained only through solution of the constituents. The change in condition preceding the formation of a fatigue crack thus appears to be similar to the change produced by a rise in temperature. The broken curve in Fig. 3 (l) shows a restoration of the state represented by Fig. 3 (b) by a further 10^7 cycles at an alternating strain of 42.5×10^{-4} . If small cracks had formed during the first 10^7 cycles, the second 10^7 cycles

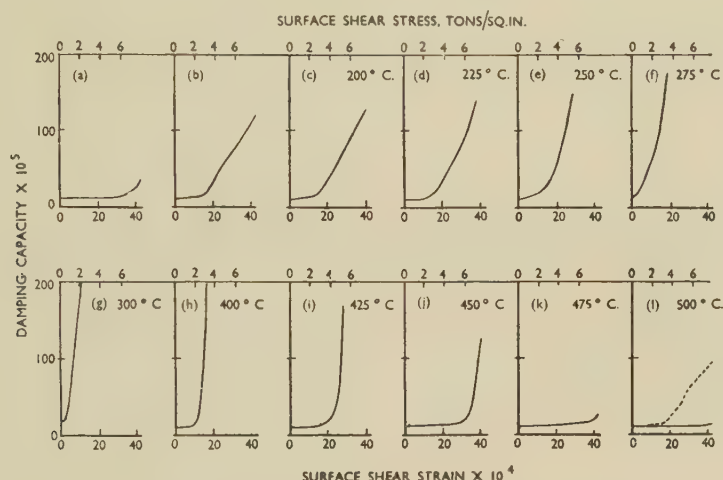


FIG. 3.—Recovery of Alloy L65 from the Effect of Vibration. Damping/Strain Curves: (a) for a fully heat-treated alloy; (b) after 10^7 cycles at a strain of 42.5×10^{-4} ; (c)–(g) after the specimen in condition (b) had been heated for 2 hr. at the temperatures shown, and then quenched in water at 20° C.; and (h)–(l) after specimen in condition (b) had been heated for 2 hr. at the temperatures shown, quenched in water at 20° C., and then aged for 6 hr. at 185° C. The broken curve in (l) shows the result of a second period of vibration as specified in (b).

specimen, originally in the fully heat-treated condition, for which the dependence of damping on strain is shown in Fig. 3 (a) up to a strain of 42.5×10^{-4} . After subjecting the specimen to 10^7 cycles at this strain, thus bringing it to a condition corresponding approximately to that of Specimen No. 3 (Fig. 2), the damping varied with strain as shown in Fig. 3 (b). On heating the specimen for 2 hr. at temperatures of 200°, 225°, 250°, 275°, and 300° C., with intermediate quenching at 20° C., followed by a determination of the variation of damping with strain, the curves shown in Fig. 3 (c), (d), (e), (f), and (g), respectively, were obtained.

Raising the temperature to these levels produced no sign of a reversion to the original unvibrated condition, and it is therefore unlikely that the effect of alternating strain is to induce locked-up stresses in the alloy. At temperatures of 250°–300° C., growth of the precipitate occurs, and Fig. 3 (e)–(g) suggests that the condition induced by alternating strain, Fig. 3 (b), is a transition state between the precipitation-hardened and the annealed conditions.

would almost certainly have produced a major fatigue crack.

If the effects of alternating strains within the fatigue range are similar to those produced by a rise in temperature, the strain/damping curve for L65 in the solid-solution state should be changed by cyclic straining so that it approaches the characteristic curve for the thermally aged alloy. Curve 3 in Fig. 4 (a) is the strain/damping curve for the thermally aged condition, and Curve 1 shows the relation obtained immediately after quenching the alloy from 500° C. In the quenched condition the damping of the specimen increases substantially when the alternating strain exceeds 20×10^{-4} . On continued cyclic straining with constant power supplied to the resonant system, the damping falls and the strain increases gradually, as shown in Fig. 4 (b).

After 30 min., corresponding to 1.62×10^6 cycles, the specimen was allowed to rest for 16 hr., during which time some ageing occurred at room temperature. On resuming cyclic straining under the same conditions of excitation, the strain was greater than at the

beginning of the rest period and increased still further during 52 min. (2.16×10^6 cycles). Thus in a total of 82 min., 4.4×10^6 cycles of strain, gradually increasing from 20×10^{-4} to 30×10^{-4} , produced a change in the same direction to approximately twice as great an extent as that caused by room-temperature ageing for 16 hr. The dependence of damping on strain after the 4.4×10^6 cycles of gradually increasing strains shown in Fig. 4(b) is given by Curve 2 in

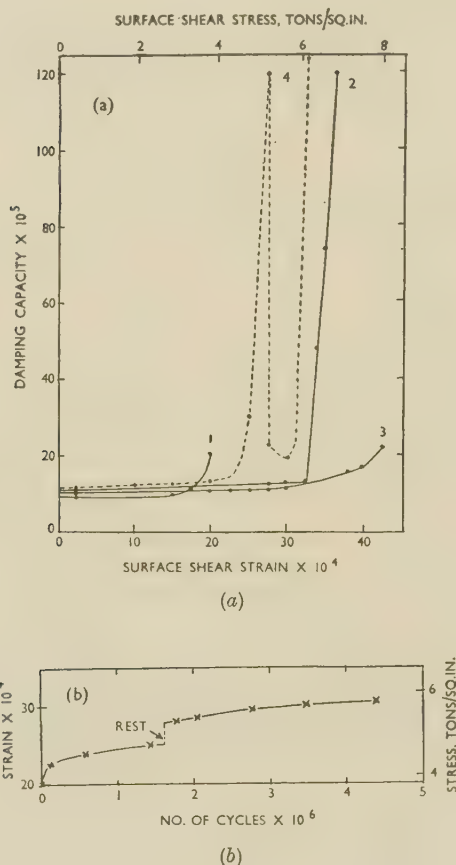


FIG. 4.—Effect of Vibration on Alloy L65 in the Solid-Solution State.

- (a) Strain/Damping Curve in: 1. alloy as quenched; 2. after vibration of 1; 3. after ageing at 185°C .; and 4. during vibration of 1.
(b) Vibration conditions preceding determination of Curve 2.

Fig. 4(a). This curve almost coincides with Curve 3 (the thermally aged alloy) for strains up to about 30×10^{-4} , the maximum strain reached during the period of cyclic straining. When this strain was exceeded, the damping increased very sharply to values far above those of Curve 3. This divergence suggests that the precipitation-hardening induced by cyclic straining is not uniform, but, for a given strain, occurs only in certain localities, perhaps in particular grains. If the strain exceeds the level of pre-straining, new localities may be activated to contribute a damping that is initially characteristic of the unvibrated alloy.

The activation of new regions by increasing the cyclic strain may also be inferred from Fig. 4(a), Curve 4, which was obtained soon after quenching a specimen of alloy L65 from 500°C . On exceeding a strain of 20×10^{-4} the damping rose sharply and then fell rapidly to a low value while the strain was held steady for the damping measurement to be made. A further increment of strain gave a repetition of the sharp rise and subsequent fall in damping.

Thus the tests on L65 alloy, both in the quenched and in the thermally precipitation-hardened states, suggest that cyclic straining within the fatigue range has an effect similar to, but more localized than, that produced by thermal ageing.

VI.—DIRECT EVIDENCE OF THE INSTABILITY OF D.T.D. 683 ALLOY WHEN SUBJECTED TO ALTERNATING STRAINS

No metallographic evidence for a change in the state of precipitation in alloy L65 after cyclic straining was found at the time of the observations described in the previous section. Later, however, changes in damping similar to those shown in Fig. 2 were found to precede fatigue failure of the D.T.D. 683 alloy.

On completion of a torsional fatigue test on a specimen of D.T.D. 683 alloy, a few fine longitudinal lines differing from the general appearance of the polished surface and not associated with the fatigue crack were observed. These lines are seen under low magnification in Fig. 5 (Plate III) to consist of a large number of short circumferential cracks.

Observations on other specimens showed that a few fine cracks appeared at the same time as the appreciable rise in damping that precedes the development of a major fatigue crack. It is difficult to obtain a reproducible photograph of these fine cracks in an early stage of formation when they have a length of 0.025–0.05 mm. Fig. 6 (Plate III) shows examples of the cracks at a later stage where their length is about 0.2 mm. This figure shows that two cracks circumferentially in line have become multiple cracks. They appear to represent an early stage in the formation of a major crack, of which Fig. 7 (Plate III) is an example.

The small cracks provide a good indication of the regions in which the expected precipitation effects of cyclic straining occur. Fig. 8 (Plate IV) is a section showing a crack that has penetrated to a depth of 0.030 mm. The section, polished and etched, shows a band of precipitation associated with the crack and an adjacent band of precipitation in which the formation of a crack is imminent if it has not already started. Solution-treatment at this stage removes the precipitation band, but does not heal the crack. The precipitation bands lie in planes of shear and, as shown in Fig. 8, form preferentially in certain grains, although the crack may propagate through a grain in which precipitation occurs only to a minor degree. Figs. 9, 10, and 11 (Plate IV) show earlier stages in the formation of the precipitation

bands, and there seems to be no doubt that they do precede the formation of the cracks.

It remains to be shown that the increase in damping preceding complete fatigue failure of D.T.D. 683 alloy is due to precipitation and not to the formation of the fine cracks that develop in the precipitation bands. During vibration of a specimen for 10^8 cycles at a strain of 42.5×10^{-4} the damping capacity increased from 6.2×10^{-5} to 11.9×10^{-5} , but no fine cracks were formed. The strain was then raised to 48.2×10^{-4} and vibration continued for a further 0.38×10^6 cycles, during which the damping rose from 15.1×10^{-5} to 436×10^{-5} . On examining the surface of the specimen, a number of fine cracks were found. After heat-treating the specimen under the conditions specified in Section III to remove any precipitation induced by the cyclic straining, the damping at a strain of 48.2×10^{-4} rose during 0.14×10^6 cycles from 10×10^{-5} to 200×10^{-5} before a major fatigue crack formed. The fall in damping from 436×10^{-5} to 10×10^{-5} as a result of further heat-treatment shows conclusively that the rise in damping which precedes fatigue failure is due mainly to precipitation induced by cyclic straining.

VII.—CONCLUSIONS

These observations suggest that aluminium alloys deriving their high static strength from controlled precipitation from solid solution are unstable under

cyclic stresses that produce fatigue. The nature of the change produced by cyclic stressing is similar to that induced by ageing at a temperature higher than that giving the maximum static strength. Whereas thermal over-precipitation produces a uniform deterioration of the alloy, cyclic stressing causes precipitation only in localized regions, possibly grains that react to the mode of stressing. Although the static strength of the material as a whole may not be impaired, the localized bands of precipitation produced by cyclic stressing are low-strength regions within which fatigue cracks form.

The fatigue strength is probably determined by the magnitude of the cyclic stress necessary to initiate precipitation and by the strength of the regions affected by over-precipitation. An alloy that is dependent for its high strength on a state of precipitation unstable under cyclic stressing will have a high ratio of static strength to fatigue strength.

ACKNOWLEDGEMENTS

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REFERENCE

1. R. F. Hanstock and A. Murray, *J. Inst. Metals*, 1946, **72**, 97.

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The synopsis should indicate newly observed facts, conclusions of an

experiment or argument and, if possible, the essential parts of any new theory, treatment, apparatus, technique, &c.

It should contain the names of any new compound, mineral species, &c., and any new numerical data, such as physical constants; if this is not possible, it should draw attention to them. It is important to refer to new items and observations, even though some are incidental to the main purpose of the paper; such information may otherwise be hidden, though it is often very useful.

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THE AGEING CHARACTERISTICS OF SOME TERNARY ALUMINIUM-COPPER-MAGNESIUM ALLOYS WITH COPPER:MAGNESIUM WEIGHT RATIOS OF 7:1 AND 2.2:1*

1560

By H. K. HARDY,† M.Sc., Ph.D., A.R.S.M., A.I.M., MEMBER

SYNOPSIS

To extend the results of work on the binary aluminium-copper alloys (*J. Inst. Metals*, 1951, 79, 321; 1953-54, 82, (6), 236) and to explore the mechanism of precipitation, an investigation has been undertaken into the ageing characteristics of two series of ternary aluminium-base alloys containing copper and magnesium in the proportions 7:1 and 2.2:1, respectively.

Hardness/ageing-time curves were obtained at 30°, 110°, 130°, 165°, 190°, 220°, 240°, and 260° C. At 110° and 130° C. the more highly alloyed materials of the 7:1 series showed two flat plateaux of relatively constant hardness, separating three hardening stages; while two-stage ageing curves (one flat plateau) occurred up to 220° C. Alloys from the 2.2:1 series (approximately pseudo-binary aluminium-S (Al_2CuMg) phase) gave one flat plateau on the ageing curves up to 240° C. The first stage of hardening occurred very rapidly and led to extremely lengthy flat plateaux. Three-stage ageing curves were not encountered in this series. Owing to the rapidity of the first rise in hardness, however, the distinction became somewhat arbitrary, as a second plateau might have been present at ageing times shorter than those investigated.

It was not possible to synthesize the ageing curves for alloys in the 7:1 series by combining the results from the 2.2:1 series and the earlier results on binary alloys. Metastable solubility curves for the decomposition product responsible for the flat plateaux were shifted to higher temperatures as the magnesium content was raised. In the ternary section the solubility curves approach the binary aluminium-copper side at a very shallow angle. The greatly increased supersaturation with respect to this decomposition product accounts for the fact that small additions of magnesium accentuate and accelerate the ageing of aluminium-copper alloys at room and slightly elevated temperatures.

The form of the ageing curves explains why reversion to the quenched hardness becomes more difficult with increasing magnesium content. The pseudo-binary aluminium-S phase alloys gave flat plateaux up to at least 240° C., which may be expected to limit the fall in hardness on a reversion treatment. At 260° C. the rise to peak hardness occurs very rapidly, which again militates against the possibility of successful reversion.

I.—INTRODUCTION

THE period of more than forty years since Wilm¹ observed that quenched aluminium-copper-magnesium alloys hardened during storage at room temperature has seen the development of the Duralumin-type alloys, with their wide and useful range of mechanical properties. A considerable amount of data has been compiled on their strength and technical ageing characteristics, and the call for ever-increased performance has also stimulated work on the equilibrium constitution. So far, however, the precipitation process has defied an accurate interpretation, and knowledge of the metastable decomposition products has accumulated only slowly. On the basis of work in many countries a satisfactory descriptive theory has been formulated for the ageing process in binary aluminium-copper alloys.²⁻⁷ A suitable extension of this work is provided by an investigation of the ageing characteristics of ternary aluminium-copper-magnesium alloys. It was thought that this would

also prove a useful step towards determining the decomposition process in Duralumin-type materials.

II.—PUBLISHED WORK

The paucity of the work already carried out on the ageing characteristics of ternary aluminium-copper-magnesium alloys rendered it desirable to consider first the results obtained on alloys of normal commercial purity, which generally contain silicon, iron, and manganese. A review of this nature would make it possible to decide whether experimental work limited to the pure ternary system could explain all the effects observed in the ageing behaviour of the more complex industrial alloys.

1. CONSTITUTION

The constitution of the ternary aluminium-copper-magnesium alloys has been admirably reviewed by Brommelle and Phillips.⁸ The α solid solution in the range of interest to the present work is in equilibrium

* Manuscript received 9 December 1953.

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with CuAl_2 , which has a negligible solubility for magnesium, and with the S phase, best represented by Al_2CuMg (see Fig. 1). The $\alpha/(\alpha + S)$ phase boundary^{9, 10} obeys mass-action principles as though

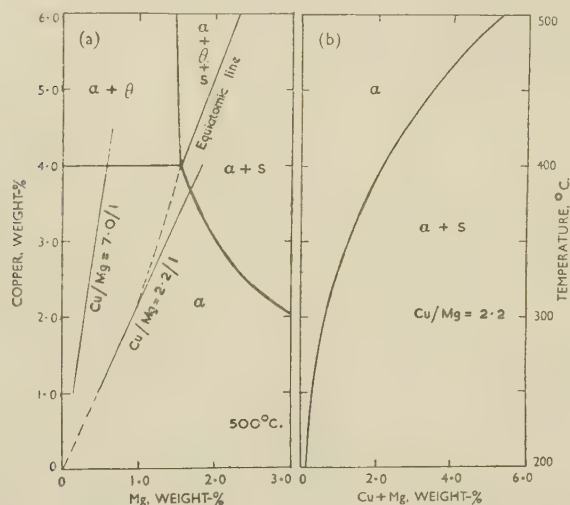


FIG. 1.—Phase Boundaries in the Aluminium-Copper-Magnesium System. The $\alpha/(\alpha + S)$ boundaries were calculated from equation (1).

in equilibrium with a binary compound.^{11, 12} The solubility data of Little, Hume-Rothery, and Raynor⁹ suggest that their equation (2) would be better written:

$$\log_{10}[\text{Cu}][\text{Mg}] = 5.603 - 3975/T \quad (1)$$

where $[\text{Cu}]$ and $[\text{Mg}]$ are the atomic percentages and T is the absolute temperature. Equation (1) has been used to plot the 500°C. isothermal in Fig. 1 (a) ending at the apex of the $(\alpha + \theta + S)$ phase field at the equiatomic composition with a copper : magnesium weight ratio of 2.61 : 1. According to Brommelle and

Phillips⁸ the apex of the three-phase field follows the dashed curve in Fig. 1 (a) as the temperature is lowered,^{9, 10} although other workers¹³⁻¹⁵ have favoured points with a higher copper : magnesium ratio.

Kuznetsov and Guseva¹⁴ found that a copper : magnesium weight ratio of 1.9 would give alloys showing no alteration from the lattice parameter of aluminium. Extrapolation from the results of Axon and Hume-Rothery¹⁶ for the apparent atomic diameters in aluminium, suggests that the contraction due to copper will be balanced by the expansion due to magnesium at ratios of 1.3 : 1 or 2.1 : 1, depending on whether their smaller or larger value be taken for magnesium. All the results suggest that magnesium has to be in excess of the equiatomic ratio.

CuAl_2 is tetragonal, with twelve atoms in the unit cell ($a = 6.045$, $c = 4.864$ kX).¹⁷⁻¹⁹ Obinata and Mutuzaki²⁰ suggested from Debye-Scherrer patterns that the S phase is also tetragonal, with $a = 5.71$ and $c = 7.94$ Å. This is not in accordance with the single-crystal work of Perlitz and Westgren,²¹ who stated that Al_2CuMg is orthorhombic with sixteen atoms in the unit cell ($a = 4.00$, $b = 9.23$, $c = 7.14$ Å.).

It is not intended to review the constitution of the quaternary aluminium-copper-magnesium-silicon alloys. It should be noted, however, that three additional phases may be introduced: elemental silicon, Mg_2Si , and a quaternary phase Q_{Si} .²²⁻²⁷ Petrov²⁸ deduced a formula for this, $\text{Al}_2\text{Cu}_4\text{Mg}_5\text{Si}_4$, but Phragmén²⁵ gave $\text{Al}_5\text{Cu}_2\text{Mg}_8\text{Si}_6$, with a hexagonal structure ($a = 4.04$, $c = 10.30$ kX).

2. AGEING CHARACTERISTICS

The published data are summarized in Tables I-III. The comparisons generally apply to a constant copper content and are valid only within the limits of composition quoted.

TABLE I.—Summary of Published Information on the Ageing Characteristics of Duralumin-Type Alloys at Room Temperature.

Item	Authors	Composition, %					Results
		Cu	Mg	Si	Fe	Mn	
1	Gayler and Preston ^{29, 30}	2 and 4	0.5	0.01 and 0.3	... *	Nil	The quenched and aged hardness values were substantially independent of the Si content.
2	Schmid and Wassermann ³¹	4.51 4.07	0.51 0.53	0.04 0.31	0.04 0.08	Nil „	The alloy with higher Si and lower Cu aged more rapidly.
3	Meissner ³²	4.2	0.5	0 and 0.3	0 and 0.3	0 and 0.6	Si had no effect on ageing.
4	Nishimura ³³	0.3-6.7	0-11.2	... *	... *	?	Max. hardening at 4% Cu occurred with 1.5% Mg; ascribed to precipitation of the S phase.
5	Nishimura ³⁴	2.5-4.4	0-1.6	Up to 0.8	... *	?	Si did not accelerate ageing at room temp. The resistivity increased during ageing.
6	Petrov ³⁵	1, 2, 3 or 4	0-1.6	0.3	0.15	Nil	Max. hardness increment in 6 days occurred with 0.6-0.8% Mg.
7	Petrov ³⁶	4.0	Mg + Si = 0.47, 0.94, 1.47		0.03	Nil	Max. hardening did not occur at the Mg : Si ratio of 2 : 1.

TABLE I.—continued.

Item	Authors	Composition, %					Results
		Cu	Mg	Si	Fe	Mn	
8	Petrov ³⁶	0.4-0 0.4-0	0.1-5 0.1-5	0.03 0.24	0.03 0.12	Nil „	The higher Fe and Si had no influence on ageing during 6 days at room temp.
9	Hansen and Dreyer ³⁷	4.0 3.0 2.0	0.5-1.9 0.5-2.1 0.5-3.3	} 0.2	0.3	0.7	Max. strength increment for Cu levels of 4, 3, and 2% occurred with 0.5, 0.8, and 1.3% Mg, respectively.
10	Hansen and Dreyer ³⁸	1.0-4.2	0.5-5.1		0.3	0.6	With >2% Mg ageing took longer to complete.
11	Hansen and Dreyer ³⁹	3.7-4.7 †	0.3-0.7 †		... *	0.3-0.7 †	This range of Si content had only a slight influence on ageing.
12	Hansen and Dreyer ³⁹	3.5-4.5 †	0.8-1.4	0.1-1.2	... *	0.9-1.5 †	Max. strength for alloys with 0.8, 1.0, 1.2, and 1.4% Mg was obtained with 0.6, 0.5, <0.1, and <0.1% Si, respectively.
13	Dreyer and Hansen ⁴⁰	2	0.5-4.0	0.2	... *	0.7	Up to 1.3% Mg accelerated ageing. Max. strength was given by 3% Mg, but represented only a slight improvement over 1.5% Mg.
14	Dreyer and Hansen ⁴⁰	1.9	1.7	0.25-2.1	... *	0.7	A change from 0.25 to 0.7% (or higher) Si content speeded up ageing, but reduced final strength properties.
15	Dreyer and Hansen ⁴⁰	0.4	0.8	1.0	... *	0.7	Strength increased linearly with Cu content.
16	Dreyer and Hansen ⁴⁰	1.4-2.0	0.8-1.4	0.65-1.0	... *	?	Rate of ageing independent of Mg ₂ Si content.
17	Dreyer and Hansen ⁴¹	3.0	0.5, 1.3, 2.1, 3.2	0.2	0.2	0.7	Max. strength at 2% Mg but max. rate of ageing at ~1%.
18	Dreyer and Hansen ⁴¹	3.0	1.6	0.17-0.86	0.2	0.6	Si had little effect on the rate of ageing, but reduced tensile values.
19	Bresson ⁴²	2.0 3.0 4.0	0.3 0.6 1.2	0.15 0.3 0.6	} ... *	Nil	Strength little affected by Si, except at the highest Mg level where it tended to be reduced by high Si.
20	Dreyer ⁴³	3.9	0.2-0	0.1	0.4	Nil	Max. rate and increment on ageing at 0.8% Mg.
21	Sharma ⁴⁴	4.4	Nil	0.1-5	Nil	Nil	Hardening reduced by increasing Si.
22	Sharma ⁴⁴	4.4	0.3-7	Nil	Nil	Nil	Max. hardening at 0.7-1.5% Mg.
23	Sharma ⁴⁴	4.4	0.4-1.5	0.4-1.5	Nil	Nil	Si had no effect on Mg-bearing alloys.
24	Fraenkel and Scheuer ^{45, 46}	4.5 ‡	0.5 ‡	... *	... *	0.5 ‡	Electrical resistance increased on ageing.
25	Igarashi ⁴⁷	0.4-0 4 4.02	0.5 0.5 0.76	... * ... * 0.69	... * ... * 0.85	Nil „ 0.32	Alloys with Cu and Mg (and Duralumin) showed an expansion followed by a contraction.
26	Eucken and Warrentrup ⁴⁸	4	0.5	... *	... *	Nil	Electrical and thermal resistance increased on ageing.
27	Fink, Smith, and Willey ⁴⁹	4.0	0.1-5	Nil	Nil	Nil	The binary alloy with Cu contracted at 30° C.; alloys with 1.0 and 1.5% Mg gave a large expansion between 1 and 10 hr., followed by a contraction.
28	Althof ⁵⁰	2.58 4.61	1.63 0.46	0.02 0.32	... * 0.38	0.62 0.46	Both alloys expanded on ageing at room temperature. Stretching the 4.6% Cu alloy immediately after quenching converted the expansion on ageing into a contraction.

* This element was present, but the amount was unrecorded. † Compositional range of specification quoted in original paper.

‡ Nominal composition; no record of analysis.

TABLE II.—Summary of Published Information on the Ageing Characteristics of Duralumin-Type Alloys at Elevated Temperatures.

Item	Authors	Composition, %					Results
		Cu	Mg	Si	Fe	Mn	
1	v. Zeerleder and Bosshard ⁵¹	3	0-1.0	0.7	0.3	Nil	Max. strength when aged at 160° C. occurred with 0.7% Mg.
2	Gayler and Preston ^{29, 30}	2.0 and 4.0	0.5	0.01 and 0.3	... *	Nil	The higher-Si alloys had peak-hardness values at 200° C. about 40 B.H.N. higher than the low-Si alloys.
3	Kempf and Dean ⁵²	4 4	0.6 0.6	0.05 0.43	0.05 0.55	Nil ,,	Peak-hardness values at 200° C. were about 35 B.H.N. higher in the alloy with 0.43% Si.
4	Meissner ⁵³	4.2 4.40	0.5 0.54	0.3 0.79	0.3 0.25	0.25 0.6	The higher-Si alloy gave slightly higher proof stress but appreciably higher U.T.S. when aged 20 or 40 hr. in the range 150°-175° C.
5	Meissner ⁵⁴	4.40	0.54	0.79	0.26	0.6	Max. corrosion after 20 hr. in the range 125°-150° C.
6	Nishimura ³⁴	2.5-4.4	0-1.6	Up to 0.8	... *	?	Two-stage ageing curves shown at 150° C. with about 4% Cu, 1.2-1.6% Mg, and 0.5-0.8% Si. The same alloys with very low Si did not give two-stage curves within the max. ageing period of 10 hr. The electrical resistivity of all these alloys increased at 150° C. but tended to fall when the second stage was reached.
7	Brenner and Kostrom ⁵⁵	3.5-4.5 † 3.7-4.7 †	0.9-1.5 † 0.4-1.0 †	0.2-0.9 † 0.1-0.7 †	0.5 † 0.5 †	0.9-1.5 † 0.3-0.7 †	The proof stress/ageing curves at 150° C. for both alloys showed two marked stages when aged immediately after quenching. On ageing at 150° C., after 7 days at room temp., the proof-stress values diminished slightly to those along the flat and then increased along the second stage of ageing to the same peak value and peak time.
8	Petrov ³⁶	4.0	Mg + Si = 0.47, 0.94, 1.47		0.03	Nil	Max. hardening at 200° C. required approximately equal quantities of Mg and Si.
9	Cohen ⁵⁶	4.19	0.58	0.14	0.32	0.63	Two-stage hardness/ageing curves obtained at 65° and 100° C. Three-stage curves obtained at 150° and 191° C. The electrical resistance first increased on ageing at all temperatures up to 191° C. but fell during the third rise in hardness (to peak) at 150° and 191° C.
10	Lindsay and Norton ⁵⁷	3.98	0.82	0.22	0.70	0.51	Three stages observed in the hardness/ageing curve at 190° C. The resistivity fell during the final (third) rise to peak hardness.
11	Hansen and Dreyer ³⁸	1.0-2.0	0.5-4.0	0.2	0.3	0.6	Weak indications of two-stage ageing curves obtained at 200° C.
12	Hansen and Dreyer ³⁹	3.5-4.5 †	0.9-1.5 †	0.1-1.2	0.5 †	0.9-1.5 †	Higher Si increased the strength after ageing at 160° C. and slightly reduced the time to peak properties. Si contents of about 1% gave more rapid over-ageing.
13	Hansen and Dreyer ³⁹	3.7-4.7 †	0.4-1.0 †	0.2-1.25	0.5 †	0.3-0.7 †	Max. strength when aged at 160° C. was given by 0.9% Si.

* This element was present, but the amount was unrecorded.

† Compositional range of specification quoted in original paper.

‡ Nominal composition; no record of analysis.

TABLE II.—continued.

Item	Authors	Composition, %					Results
		Cu	Mg	Si	Fe	Mn	
14	Hansen and Dreyer ³⁹	3·5–4·5 †	0·9–1·5 †	0·1, 0·6, 1·0	0·5 †	0·9–1·5 †	Cold work from 0–10% before ageing at 160° C. always increased the max. proof-stress value. The proof-stress increment on ageing was raised for the 0·1% Si alloy, but no effect was noticeable at the 0·6% Si level. With 1·2% Si cold work decreased the proof-stress increment, so that the highest proof stress after cold work and ageing was given by the 0·6% Si alloy.
15	Dreyer and Hansen ⁴⁰	2·0	0·8, 1·5, 3·0	0·2	... *	0·7	Peak proof stress at 150° C. occurred after about 600 hr. in all cases.
16	Dreyer and Hansen ⁴⁰	1·9	1·7	0·25–2·1	... *	0·7	Higher Si contents favoured higher strengths and shorter times to peak properties. With 1·2–2·1% Si 100 hr. were required at 160° C.
17	Dreyer and Hansen ⁴⁰	0·4–0	0·8	1·0	... *	0·7	Strength increased linearly with Cu content when aged 5 hr. at 170° C.
18	Dreyer and Hansen ⁴¹	3·0	0·5–2·1	0·2	0·2	0·7	At 240° C. peak hardness was higher and reached more rapidly as the Mg content was raised.
19	Dreyer and Hansen ⁴¹	3·0	1·6	0·17–0·86	0·2	0·6	On ageing at 160° C. the max. proof stress was higher and reached more quickly with higher Si contents.
20	Borchers and Castellani ⁵⁸	2·6	1·80	0·29	0·4	0·65	Two-stage ageing curves obtained at 200° C.
21	Sharma ⁴⁴	4·4	Nil, 0·4–3·7	Nil	Nil	Nil	Ternary alloys with 4·4% Cu and 0·4, 0·7, and 1·5% Mg gave evidence of two-stage ageing curves at 160° C. because a very rapid hardness rise at the start of ageing was followed by a more gentle rise to peak hardness. The 4·4% Cu alloy with 2 and 3·7% Mg gave very long flat peaks extending from 2 to 30 hr. at 160° C.
22	Sharma ⁴⁴	4·4	0·4–1·5	0·4–1·5	Nil	Nil	Although Si had little effect on max. hardness at 160° C., the time to peak hardness was reduced.
23	Sharma ⁴⁴	4·4	Nil	0·4–1·5	Nil	Nil	Max. hardness at 160° C. was slightly reduced by Si additions.
24	Laurent and Jarlan ⁵⁹	4·1	1·15	0·55	0·5	0·65	Weak indications of several stages in the ageing curves.
25	Jackman, ⁶⁰ Mitchell, ⁶¹ Mozley, ⁶² Tatman and Miller ⁶³	4·5 †	1·5 †	... *	... *	0·6 †	Cold work before ageing raised strength.
26	Fritzlen and Mondolfo ^{64, 65}	4·5 †	0·4 †	1·0 †	1·0 †	0·2–0·8 †	Cold work before ageing did not appreciably alter final properties.
27	Kästner ⁶⁶	2·0	0·75	1·0	... *	0·6	Combinations of stretching and ageing at 175° C. were studied.
28	Gunn ⁶⁷	4·5 † 4·3 † 4·3 †	1·5 † 1·0 † 0·5 †	... * ... * 0·75 †	... * ... * ... *	0·6 † 0·75 † 0·75 †	Increase of proof stress due to 40% cold work before ageing was respectively 40, 40, and 10% for alloys listed.
29	Robertson ⁶⁸	4·55	1·50	0·15	0·24	0·66	Slight softening at beginning of artificial ageing but no other indication of two-stage ageing curves. Max. susceptibility to corrosion occurred towards the end of the succeeding incubation period.
30	Logan, Hessing, and Francis ⁶⁹	4·4	1·45	0·23	0·34	0·60	Max. susceptibility to corrosion after short ageing times.

TABLE III.—Summary of Published Information on the Reversion Characteristics of Duralumin-Type Alloys.

Item	Authors	Composition, %					Results
		Cu	Mg	Si	Fe	Mn	
1	Gayler, ^{70, 71, 72}	... §	... §	... §	... §	Nil	Several alloys softened when heated for short times at elevated temperatures after ageing at room temperature.
2	Teed ⁷³	4.49	0.65	0.21	0.42	0.69	The alloy, aged at room temperature, softened slightly on heating 1½ hr. at 160° C. and did not recover after a further 17 weeks at room temperature.
3	Brenner and Kostron ⁵⁵	3.5-4.5 † 3.7-4.7 †	0.9-1.5 † 0.4-1.0 †	0.2-0.9 † 0.1-0.7 †	0.5 † 0.5 †	0.9-1.5 † 0.3-0.7 †	Ageing at 150° C. after 7 days at room temperature reduced the proof stress to the value obtained along the flat when aged immediately after quenching. The initial fall in proof stress at 150° C. was more pronounced the greater the cold work before ageing.
4	Dreyer ⁷⁴	4.28	0.53	0.27	0.33	0.6	Complete softening obtained with short heatings at 220° and 240° C. Lower temperatures gave partial softening and slow re-ageing. Cold work reduced the hardness fall on reversion.
5	Dreyer ⁷⁵	4.2 †	0.5 †	0.3 †	0.3 †	0.6 †	Almost complete reversion obtained by treating at 240° C. Cold work reduced the fall in hardness on reversion.
6	Dreyer and Hansen ⁴¹	3	0.5-2.1	0.2	0.2	0.7	Short-time heating at 240° C., produced less softening the higher the Mg content. Re-ageing at room temperature also took longer the higher the Mg content.
7	Dreyer ⁷⁶	3.75	0.8, 1.1, 1.3	0.06	0.08	1.1	None of the materials returned to the quenched hardness on reversion, but the 0.8% Mg alloy gave the greatest reduction in hardness. Cold work reduced the softening on reversion and the rate of re-ageing at room temperature; the effect was more pronounced the higher the Mg content.
8	Dreyer ⁷⁶	4.2	0.8	0.18, 0.65, 1.18	0.3	0.55	High Si interfered still further with the reversion by giving more rapid ageing at elevated temperatures.
9	Borchers and Castellani ⁵⁸	2.6	1.80	0.29	0.4	0.65	Short times at temperatures over 300° C. gave reversion from the flat on the hardness/ageing curve at 200° C. The reversionability decreased to zero at the peak.
10	Dreyer ⁴³	3.9	0.2-0	0.1	0.4	Nil	With up to 0.4% Mg all the room-temperature hardening was removed by reversion. With more than 0.7% Mg, 5 min. at 260° C. increased the hardness and led to increased hardness on re-ageing at room temperature.
11	Dreyer ⁷⁷	4.28	0.53	0.27	0.33	0.6	A difference was found in the reversion and re-ageing characteristics depending on whether the cold work was carried out immediately or after 60 days' ageing. Re-ageing of cold-worked and reverted material complete after 5 years.
12	Boone ⁷⁸	4.4 † 4.5 † 4.5 †	0.35 † 0.5 † 1.5 †	0.8 † 0.9 † ... *	... * ... * ... *	0.75 † 0.8 † 0.6 †	Recommended reversion treatment for industrial handling was 30 min. at 150° C. for the first two alloys and 10 min. at 190° C. for the last alloy. The treatment was suitable only for clad sheet subsequently fully aged, because the corrosion-resistance was lowered.

* This element was present, but the amount was unrecorded.

† Nominal composition, no record of analysis.

‡ Compositional range of specification quoted in original paper.

§ This element was present.

(a) Ageing at Room Temperature (Table I)

(i) Small amounts of magnesium accelerate and increase the extent of ageing at room temperature, but there is disagreement over the most effective copper : magnesium ratios (Items 4, 6, 9, 10, 13, 17, 20, 22 of Table I).

(ii) Small quantities of silicon have little effect on ageing at low magnesium contents (Items 1, 2, 3, 5, 8, 11, 12, 14, 18, 19, 21, 23).

(iii) The maximum strengths and ageing increments are not simply related to a unique magnesium : silicon ratio (Items 7, 12, 16).

(iv) The electrical resistance increases on ageing (Items 24, 26).

(v) The alloys with copper and magnesium expand on ageing (Items 25, 27, 28).

(b) Ageing at Elevated Temperatures (Table II)

(i) Multi-stage ageing curves may occur, depending on the alloy and ageing temperature: two-stage (Items 6, 7, 9, 11, 20, 21, 24 of Table II); three-stage (Items 9, 10). Alloys with a low copper : magnesium ratio may show two-stage ageing curves at 200° C., but a very long flat with no final peak at 160° C. (Items 1, 15, 20).

(ii) Successively higher additions of magnesium first accelerate and then retard the rate of ageing (Items 15, 18).

(iii) Silicon additions may enhance the maximum properties (Items 2, 3, 4, 8, 12, 13, 16, 19; contradicted by Items 22, 23; this depends on the magnesium : silicon ratio (Items 1, 8)).

(iv) Small and medium silicon additions accelerate the ageing (Items 12, 16, 19, 22).

(v) The electrical resistivity increases during the early stages of ageing and falls at the start of the final rise to peak hardness (Items 6, 9, 10).

(vi) The maximum susceptibility to corrosion occurs after short ageing times (Items 5, 9, 30).

(vii) The increase in strength on ageing after cold work falls as the magnesium : silicon ratio is reduced (Items 14, 25, 26, 27, 28).

(c) Reversion Characteristics (Table III)

(i) The reversion is more complete the lower the magnesium content and the lower the silicon content in the presence of magnesium (Items 4, 5, 6, 7, 8, 9, 10 of Table III).

(ii) The degree of reversion depends on the position along the ageing curve from which the reversion is carried out (Item 9).

(iii) The relation between cold work and reversion depends on the alloy composition (Items 3, 4, 5, 7).

(d) Effect of Other Elements

Iron and manganese may withhold other solute elements from solution by compound formation or by limiting the solubility. They appear to have little direct influence on the precipitation process.^{30, 35, 41, 44, 49, 79-83}

(e) Discussion

The presence of silicon increases the strength values and reduces the time to peak properties at elevated temperatures. Therefore, it will not be possible to argue from the results on the ternary aluminium-copper-magnesium alloys directly to the industrial alloys, which are essentially quaternary in their ageing behaviour. The importance of the magnesium : silicon ratio has been recognized, but cannot yet be associated with the precipitation of any particular compound.

Brenner and Kostron⁵⁵ (Items II, 6 and III, 3) have reported that their alloys aged for seven days at room temperature softened slightly on ageing at 150° C. to give properties almost identical with those along the flat plateau of the ageing curve for alloys aged immediately after quenching. This observation is very significant, because it explains many failures to observe the two-stage ageing curves. The long incubation period found at elevated temperatures, for example in Robertson's curves,⁶⁸ would then represent the flat on the ageing curve. The hypothesis that reversion cannot reduce the properties significantly below the values along the flat on the ageing curve at the reversion temperature, has been suggested for aluminium-copper alloys by Saulnier.⁸⁴ However, the evidence was not very satisfactory, particularly since the incubation value for the initial rise in this system may be much longer than the reversion time. The hypothesis seems reasonable when applied to aluminium-copper-magnesium (-silicon) alloys, which begin to age very rapidly at elevated temperatures. The difficulties experienced in reverting alloys containing magnesium and magnesium + silicon (Table III) can then be used to support the conclusion that these elements raise the temperature up to which two-stage ageing curves should be found.

The significance of the three-stage ageing curves is not fully established. Except in one instance at 150° C.,⁵⁶ the first stage occurred at ageing times which must have been of a similar order to the time for heating to the ageing temperature and may have to be associated with effects occurring during heating.

3. STRUCTURAL AGEING CHARACTERISTICS

As in the case of many other systems, the fineness of the precipitates formed at low ageing temperatures has greatly reduced the value of metallographic investigations. The precipitates become visible at higher ageing temperatures, and Gayler⁸⁵ has recorded microscopically the presence of the binary aluminium-copper compounds θ' and θ , together with a new buff-coloured phase on {100} planes of the matrix in an aluminium-4% copper-0.5% magnesium alloy, aged at 350° C. An alloy with copper 4, magnesium 0.5, silicon 0.3, iron 0.11%, aged for 28 days at 250° C. gave a different new phase whose plane of precipitation could not be determined.

Electron microscopy has not proved able to differentiate between the various precipitates and can

provide information only on the particle size and shape.⁸⁶⁻⁸⁸ According to Nishimura and Murakami^{89,90} alloys with about 3% copper and 1% magnesium give plates of precipitate on {100} and {110} matrix planes when aged in the range 200°–250° C.

The limited amount of X-ray work has been critically discussed by Hardy and Heal.⁹¹ Bagaryatsky^{92,93} used an alloy with 3% copper and 1.15% magnesium. He interpreted his results at low ageing temperatures to mean that groups of copper and magnesium atoms were formed on {100} planes of the matrix. At higher ageing temperatures, these grew on {021} matrix planes into a new intermediate structure closely analogous to the *S* phase. Bagaryatsky claimed that *S'* was orthorhombic, with $a' = 4.04$, $b' = 9.04$, and $c' = 7.2$ Å., providing a fit between (100)_{*S'*} and (021)_{Al}. A second orientation relation was possible between (011)_{*S'*} and (035)_{Al}, but required a greater distortion. It was inferred that over-ageing was associated with loss of coherency of this orientation. It is not clear why this does not facilitate the formation of the *S* phase. It should be noted that there is only a 4° difference between pairs of planes of types {021} and {035}, so that the distinction could probably not be proved metallographically. Both these planes are appreciably different from those suggested by Gayler and by Nishimura and Murakami.

Bagaryatsky gave the orientation relation between the *S* phase and the matrix as :

$$[100]_S \parallel [100]_{Al}; [010]_S \parallel [012]_{Al}; [001]_S \parallel [021]_{Al}$$

Lambot^{94,95} worked with an alloy containing 4% copper and 1.28% magnesium. The low-angle scatter technique showed evidence of copper segregation on {100} planes, which supports Bagaryatsky's interpretation. Lambot did not find re-rods* along <021> directions and did not obtain sharp *S'* reflections at 200° C., although Bagaryatsky reported them after 30 min. at 218° C. The full meaning of Lambot's checkerboard reciprocal lattice plots still has to be worked out. He was able to give only a linear relationship between the *S* phase and the matrix, namely :

$$[100]_S \parallel [100]_{Al}$$

According to Bagaryatsky, the major sequence is :

$$\begin{array}{l} \text{G.P. zones (Cu + Mg)} \\ \text{on } \{100\}_{Al} \end{array} \rightarrow \begin{array}{l} S' \text{ platelets on } \{021\}_{Al} \\ \text{and } \{035\}_{Al} \end{array} \rightarrow S$$

and there are no G.P. zones [2] (θ''), such as occur in the aluminium-copper system.^{3,4,7} However, the discrepancies clearly require more systematic work to provide a complete pattern of precipitates for all supersaturations.

Lambot^{94,95} also studied quaternary aluminium-copper-magnesium-silicon alloys, but again met with

difficulty in the interpretation of the diffraction patterns.

III.—EXPERIMENTAL PROCEDURE

In the present investigation two series of alloys were prepared with copper : magnesium weight ratios nominally 7.0 : 1 and 2.2 : 1. The relationship to the constitution is shown in Fig. 1 (*a*). At equilibrium about three-eighths of the precipitated copper in the first series of alloys would be present in the *S* phase (Al₂CuMg) and the remainder would be in the CuAl₂ phase. The second series of alloys was chosen to lie in the direction from the origin to the apex of the ($\alpha + \theta + S$) phase field at low temperatures and may be regarded as pseudo-binary aluminium-*S* phase alloys. In each series, up to seven alloys were investigated with copper contents between 1¼% and the solubility limits at 500° C.

The experimental methods adopted were identical with those used previously^{5,6,96} and will only be summarized here. Materials of the highest available purity were carefully melted and water-chill-cast to 1¼-in.-dia. billets. These were scalped, annealed, and (generally) cold forged to 0.52 in. square, homogenized, annealed, and flattened to 0.22 in. thick and 1–1¼ in. wide. The specimens were identified, 0.060 in. machined from one surface, cut and ground before heat-treatment, in order to minimize their subsequent handling, so that they only required final grinding on 00 emery paper before hardness testing.

The initial solution-treatment was for not less than 48 hr. at 505° C. in a salt bath, followed by quenching in water at 20° ± 1° C. The specimens were dried by rinsing in acetone and aged at 30°, 110°, 130°, 165°, 190°, 220°, 240°, and 260° C. The time between quenching and placing in the furnace did not exceed 5 min. The 30° C. treatment was carried out in an oil bath. Circulating-air furnaces were used from 110° to 220° C., and a salt bath at 240° and 260° C. The time for the specimens to reach a temperature 2° C. lower than that of the furnace was approximately 5 min., except for the salt baths in which the specimens required 1.5 min. These times have been allowed in plotting the ageing curves.

Five Vickers diamond pyramid hardness tests were made on each specimen after ageing. Duplicate specimens were used for each point on all the ageing curves, except that single specimens were used for times longer than 200 days at 110°–190° C. or 10 days at 220° C. Specimens were not re-aged unless their initial ageing treatment had been lengthy.

Spectrographic analysis showed no loss of magnesium from the surface during heat-treatment. After hardness testing, two specimens from each billet were analysed chemically for copper and magnesium. The averaged results are given on the graphs and show that the compositions were adequately close to the nominal copper : magnesium ratios.

* Rods of diffracted intensity in the reciprocal lattice (see Hardy and Heal⁹¹).

As in the previous work^{5, 6, 96} an incubation value has been adopted to indicate the time to the beginning of ageing. This is obtained by extrapolating the rising ageing curve back to the hardness value during the incubation period. This incubation value falls between the incubation period and the time to the maximum rate of hardening.⁵

It is most convenient to decide the number of stages in the ageing curve from the number of flat plateaux present. One plateau indicates that hardening occurs in two stages; two plateaux that it occurs in three stages.

IV.—EXPERIMENTAL RESULTS

1. TYPES OF CURVES OBTAINED

Representative ageing curves are given in Figs. 2 and 3 for all the alloys at 110° C., and in Figs. 4 and 5 for the most highly alloyed materials at ageing temperatures from 130° to 260° C.* Some of the hardness changes are summarized in Figs. 6 and 7.

(a) Ageing at 30° C.

For a given percentage of copper, the alloys with a higher magnesium content aged more rapidly and reached a higher hardness value, e.g. alloys containing about 1·3% copper showed increments of 16 and 35 V.P.N. for the 7 : 1 and 2·2 : 1 series, respectively. The rise in hardness was complete after ten days, and only slight or negligible changes occurred in the next 950 days. Previous work had indicated little and very slow hardening in a binary aluminium-2% copper alloy.

(b) Ageing at 110° C.

The alloys with a copper : magnesium ratio of 7 : 1 showed clear evidence of three-stage ageing curves at the higher supersaturations. For example, the alloys containing 3·4 and 3·55% copper (Fig. 2) hardened very considerably (from about 60 to 86 V.P.N.) either during heating to the ageing temperature or within the first 3 min. at temperature. A fairly flat portion up to about 15 min. was succeeded by a steady rise, with a further flat plateau extending from 1 to 20 days. The final rise to peak hardness was completed after some two to three hundred days. The 2·8% copper alloy showed a hardness increment of 10 points after 3 min. at 110° C., which may be a weak indication of the first stage observed at higher supersaturations. The first stage was missing at low copper contents, but clear indications were obtained of two-stage curves separated by flat plateaux.

At high supersaturations the alloys with a copper : magnesium ratio of 2·2 : 1 showed a much greater hardness increment on heating to the ageing temperature. For instance, the hardness of the alloys with 3·2 and 2·7% copper changed from 78 to 116 V.P.N.

and from 68 to 109 V.P.N., respectively, within 3 min. at temperature. The hardness changed only slightly over the following 70–90 days (Fig. 3). The rise in hardness on heating, or during the first few minutes at temperature, became less marked as the concentration was decreased. All the alloys showed two-stage ageing curves, but no evidence was obtained for three stages (only one plateau was well defined). It becomes a matter for definition whether the rise in hardness during heating be regarded as a separate stage from the subsequent slow rise to the constant value along the flat plateau. The time for the beginning of the rise to peak hardness was substantially independent of the supersaturation. It seems likely that peak hardness would be reached after 800–1300 days, but the proof would require ageing times of up to 1500–2000 days.

(c) Ageing at 130° C.

The more highly alloyed materials with a copper : magnesium ratio of 7 : 1 again gave three-stage ageing curves with two well-defined plateaux (Fig. 4). The hardness of the alloys with 3·55 and 3·5% copper increased from 60 to about 87 V.P.N. during heating, which constitutes the first stage. The hardness remained relatively constant for about 10 min., when the second stage of hardening occurred. The final stage of hardening to peak hardness started after 2 to 3 days. The alloy with 2·7% copper also gave a three-stage curve, but alloys of lower copper content showed only two stages. No flat plateaux were found in the alloys with 1·8 and 1·3% copper, in which a slow rise in hardness was followed by a more rapid rise to the peak. The times to the final incubation value and to peak hardness increased as the supersaturation was decreased.

Only one plateau occurred in the ageing curves of the 2·2 : 1 series (Fig. 5). In the alloys with 3·1 and 2·7% copper, the first stage of hardening was almost completed during or shortly after heating, the hardness changing from a quenched value of about 70 V.P.N. to about 110 V.P.N. The almost flat plateau extended to 6 or 7 days, and was followed by the rise to peak hardness which occurred after 60–65 days. As the supersaturation was decreased the time to reach the truly flat portion of the curve lengthened. The absence of a three-stage ageing curve cannot be proved, because a second plateau might occur at ageing times shorter than 3 min. The time to peak hardness was much less dependent on concentration than in the alloys with a copper : magnesium ratio of 7 : 1.

(d) Ageing at 165° C.

No evidence of three-stage ageing curves was obtained in the alloys with a copper : magnesium ratio of 7 : 1. Flat plateaux occurred in the alloys with 3·7 (Fig. 4) and 3·5% copper. Two-stage ageing

* A complete set of ageing curves has been deposited in the Joint Library of the Institute of Metals and the Iron and Steel Institute.

curves were also shown by the alloys containing 2.8 and 2.3% copper, but the flat part of the curve was not reached before the rise to peak hardness began. The alloys with 1.9 and 1.5% copper gave single-stage ageing curves in which only the rise to peak hardness occurred.

of 7 : 1 was less than at 165° C. (Fig. 4). For example, the hardness of the alloy with 3.5% copper increased by 10 V.P.N. to the flat, compared with 20 V.P.N. at 165° C. The tendency to two-stage curves decreased, and the time to peak hardness lengthened as the supersaturation was reduced.

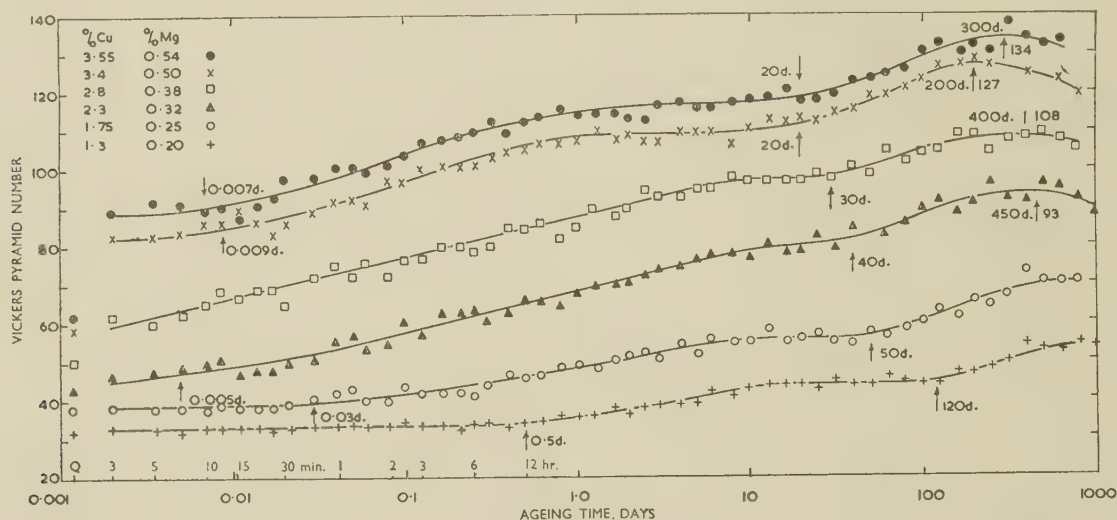


FIG. 2.—Hardness/Ageing-Time Curves at 110° C. for Alloys with a Copper : Magnesium Ratio of 7 : 1.

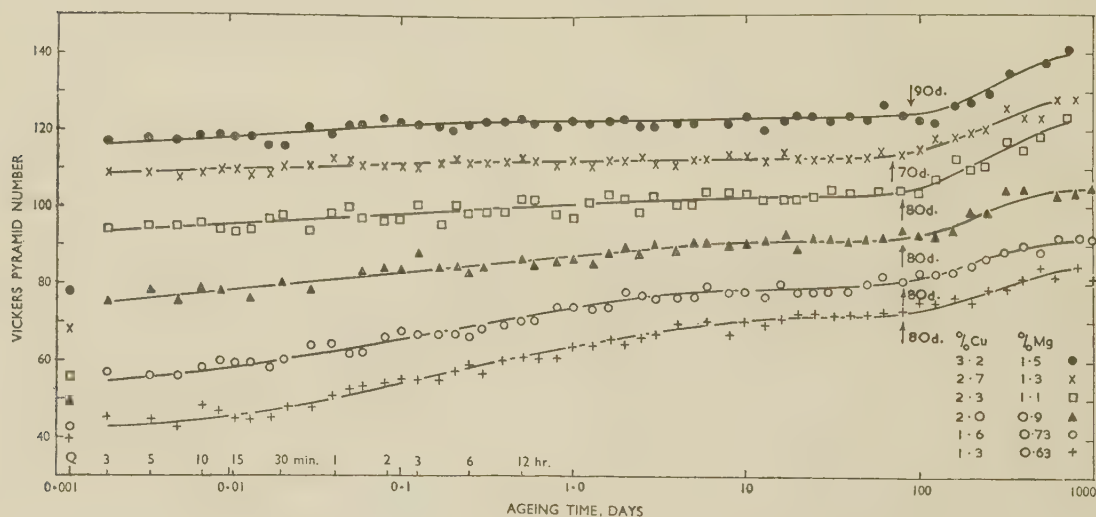


FIG. 3.—Hardness/Ageing-Time Curves at 110° C. for Alloys with a Copper : Magnesium Ratio of 2.2 : 1.

Two-stage ageing curves were again observed in all the alloys possessing a copper:magnesium ratio of 2.2:1 (Fig. 5). The time to the completion of the initial rise lengthened as the supersaturation was reduced, but the incubation values for the rise to peak hardness and the times to the peak hardness were not strongly dependent on the concentration.

(e) *Ageing at 190° C.*

The hardness increment during the first stage of ageing in the alloys with a copper : magnesium ratio

Two-stage ageing curves were obtained in all the alloys with a copper:magnesium ratio of 2.2:1. The alloy with 1.28% copper represented a boundary condition, because only a slow and not very large hardness increment occurred before the rise to peak hardness. Two-stage ageing curves with flat plateaux were clearly apparent at the higher supersaturations, where the first stage was almost completed during heating or shortly afterwards (Fig. 5). The incubation values for the final rise and the times to peak hardness were again only slightly dependent on composition in the alloys with more than 1.7% copper.

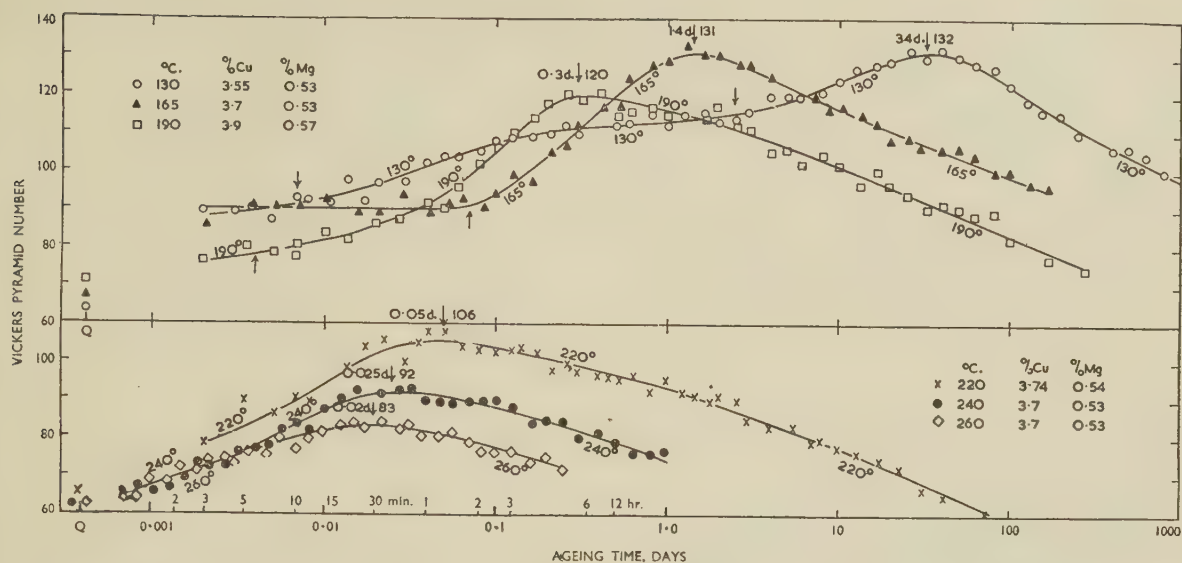


FIG. 4.—Hardness/Ageing-Time Curves at Various Temperatures for the Most Highly Alloyed Materials with a Copper : Magnesium Ratio of 7 : 1.

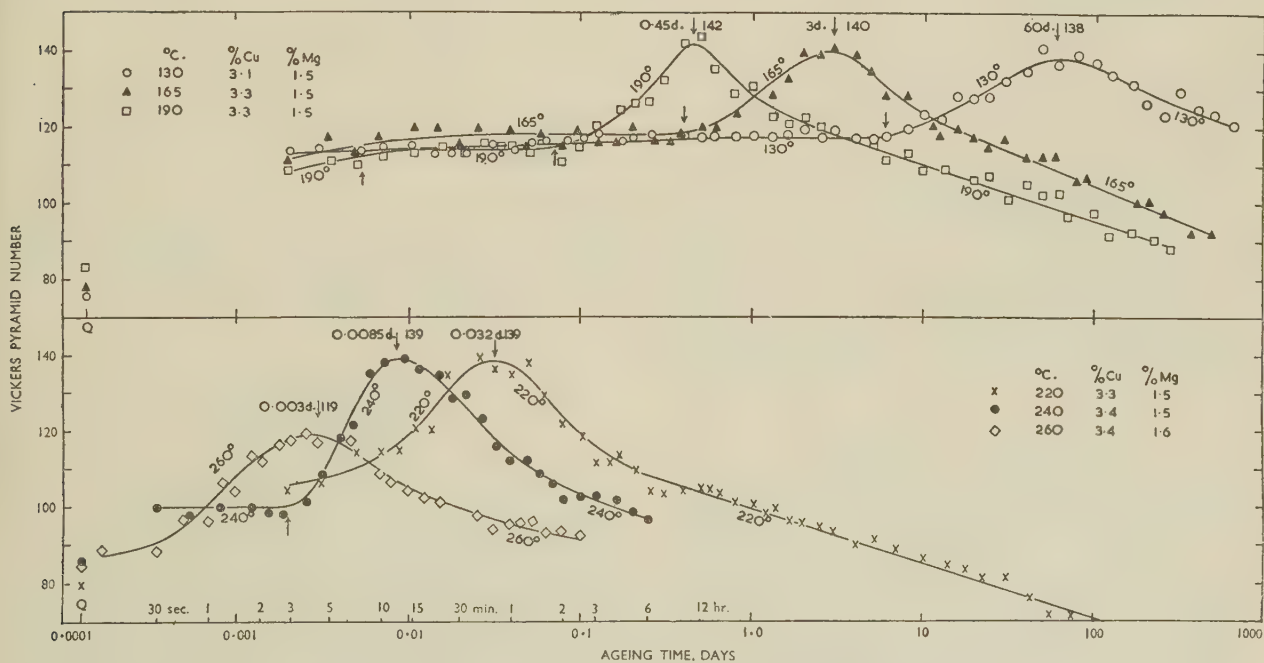


FIG. 5.—Hardness/Ageing-Time Curves at Various Temperatures for the Most Highly Alloyed Materials with a Copper : Magnesium Ratio of 2·2 : 1.

(f) Ageing at 220° C.

In the 7:1 series, the alloy with 2.85% copper possessed a flat plateau 10 V.P.N. above the as-quenched hardness. It may be inferred that similar results would probably occur in the two alloys of high supersaturation, although these were not investigated for ageing times of less than 3 min. (Fig. 4). The alloys with 2.3, 1.7, and 1.4% copper gave single-stage ageing curves.

The shape of the ageing curves for the alloys in the 2:2:1 series suggests that two-stage ageing curves were present in the alloys with down to 2.0% copper. Single-stage curves were obtained with copper contents of 1.5 and 1.35%.

(g) Ageing at 240° C.

The alloys with a copper:magnesium ratio of 7:1 gave single-stage ageing curves with gently rounded maxima (Fig. 4).

Two-stage ageing curves were obtained down to a copper content at least as low as 2.35% in the series with a copper:magnesium ratio of 2:2:1 (Fig. 5). The final incubation value and the time to peak hardness were not greatly dependent on the concentration. The hardness along the flat was again less than at lower temperatures, e.g. 92 V.P.N. in the alloy with 3.2% copper compared with 117 V.P.N. at 130° C., but the peak hardness was only slightly reduced from 138 to 132 V.P.N. in the same alloy.

(h) Ageing at 260° C.

Only slight hardening was given by single-stage ageing curves in the alloys of the 7:1 series (Fig. 4).

Single-stage ageing curves were also obtained from the alloys with 1.7 and 2.35% copper in the series with a copper:magnesium ratio of 2:2:1. It is not very obvious whether the ageing curves at the higher copper levels were single- or two-stage. The hardness values at the shortest ageing times were only slightly above the quenched values and, in any case, the ageing was too rapid to give well-marked flat plateaux (Fig. 5).

2. ANALYSIS OF RESULTS

(a) Quenched Hardness/Concentration Relationships (Figs. 6-8)

The quenched-hardness values are best represented as rectilinear functions of composition for each series of alloys. The straight lines in Figs. 6 and 7 extrapolate to 15 V.P.N. for a copper + magnesium content of zero. This is also the value to which the quenched hardnesses of the binary aluminium-copper alloys extrapolate at zero alloy content.⁵ The quenched-hardness values of the more highly supersaturated materials in the series with a copper:magnesium ratio of 2:2:1 showed a greater than normal scatter and fell above the chosen straight line of Fig. 7. This is believed to result from ageing during the test, which

occupied approximately 5 min. from the time of quenching.

The quenched-hardness values taken from the mean straight lines and from the earlier work on binary

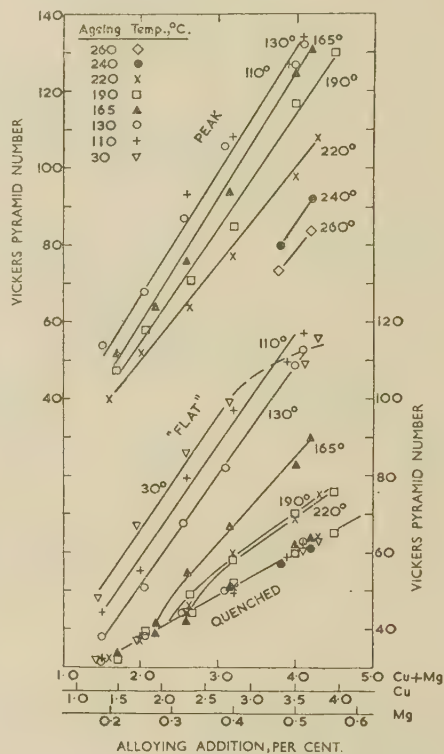


FIG. 6.—Effect of Alloying Additions on the Quenched, "Flat", and Peak-Hardness Values of Alloys with a Copper:Magnesium Ratio of 7:1.

aluminium-copper alloys⁵ are plotted at different copper levels in Fig. 8 as a function of the magnesium content. Increasing magnesium raised the quenched hardness disproportionately, so that curved relations were obtained.

(b) "Flat" Hardness/Concentration Relationships (Figs. 6, 7 and 9)

When the ageing curves did not exhibit a truly flat plateau, the hardness values were taken after a suitable ageing time before the final rise to peak hardness. When considered in broad outline, the results are reasonable and satisfactory, but appreciable scatter was recorded at some ageing temperatures. For example, the hardness values at 30° C. of the two alloys with about 3.7% copper + magnesium in the 7:1 series were appreciably lower than would be suggested by extrapolation from the less highly alloyed materials. The highest hardnesses were generally obtained at the lowest ageing temperatures, although little difference was found between the values at 190° and 220° C. in the 7:1 series, or between 110° and 130° C. in the 2:2:1 series. Results at 260° C. have been included in Fig. 7, but their validity

is not certain because the hardness values were very close to the quenched hardnesses.

The compositions at which the curves for the flat hardness values reach the quenched hardness may be

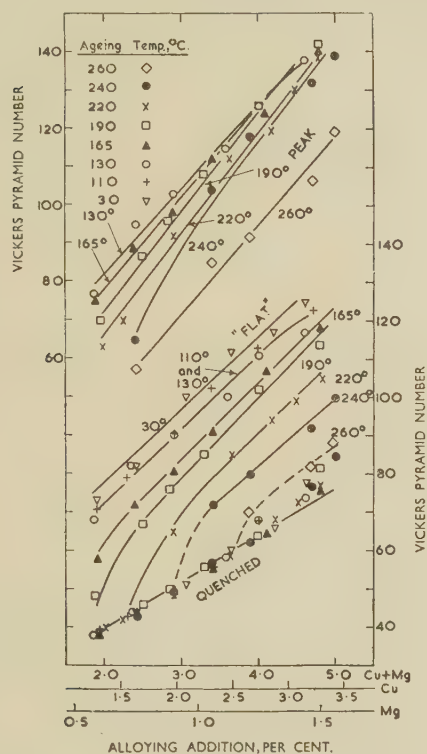


FIG. 7.—Effect of Alloying Additions on the Quenched, "Flat", and Peak-Hardness Values of Alloys with a Copper: Magnesium Ratio of 2:2:1.

taken as the solubility limits of the metastable decomposition product responsible for the flat plateaux.

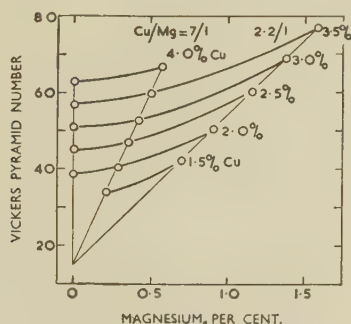


FIG. 8.—Quenched-Hardness Values of Aluminium-Copper⁵ and Aluminium-Copper-Magnesium Alloys at Different Copper Levels as a Function of Magnesium Content.

The results, together with those for the binary aluminium-copper alloys,^{5, 6} are given in Fig. 9. Decreasing the copper: magnesium ratio shifted the curves to lower alloy contents but raised the upper limit of

temperature stability. When plotted in the ternary section the solubility curves were roughly parallel to the $\alpha/(\alpha + S)$ phase boundary (see Fig. 15, p. 33).

(c) Peak Hardness/Concentration Relationships (Figs. 6 and 7)

Apart from the 2:2:1 series at 240° C., no evidence was obtained suggesting the inflected relationships such as occur in aluminium-copper alloys.^{5, 6} The

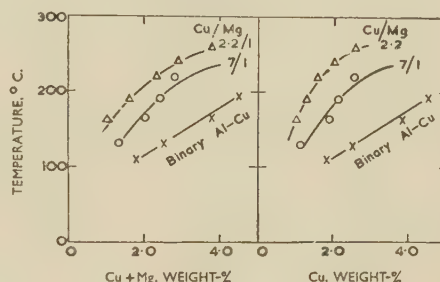


FIG. 9.—Limiting Temperature and Concentration Relationships for Metastable Decomposition Products Producing Flat Plateaux on the Ageing Curves of Quenched Alloys with Copper: Magnesium Ratios of 2:2:1 and 7:1, and of Quenched Binary Aluminium-Copper Alloys.

peak-hardness value was more temperature-dependent, particularly at high alloy contents, in the 7:1 series than in the 2:2:1 series of alloys. In both series, the hardness increment between flat and peak tended to increase as the ageing temperature was raised. For example, the alloy with 4.5% copper + magnesium in the 2:2:1 series showed a hardness increment between "flat" and peak of 17 V.P.N. at 130° and 38 V.P.N. at 240° C.

(d) Incubation Value/Temperature Relationships (Figs. 10 and 11)*

The incubation values for the rise to peak hardness plotted against $1/T$ could be represented as straight lines over a wide range of ageing temperature, although minor departures occurred in the 2:2:1 series (Fig. 11). The incubation values for a given ageing temperature occupied a much narrower time range in the 2:2:1 than in the 7:1 series. A possible C-curve for the earlier incubation values is suggested in Fig. 10. The clear indications of the C-curves found in the aluminium-copper alloys^{5, 6} were not reproduced by the ternary alloys, partly because the initial rise at high supersaturations occurred during heating or at extremely short ageing times.

(e) Time to Peak Hardness/Temperature Relationships (Figs. 12 and 13)*

The results are best represented by straight lines over a wide range of ageing temperatures. The apparent⁹¹ "activation energies" from the slopes of the curves increased from the 7:1 to the 2:2:1 series and with increasing alloy content. The binary

* The points plotted in Figs. 10-13 were obtained from the ageing curves by intrapolation.

aluminium-copper alloys had given a value of 24,000 cal./g.-atom.^{2, 5}

(f) *Synthesis of Ageing Curves* (Fig. 14)

The alloys with a copper : magnesium ratio of 7 : 1 contain both CuAl_2 and Al_2CuMg when fully precipi-

aluminium-copper alloys^{5, 6} and pseudo-binary aluminium-S phase alloys.

Assume that the quenched alloy can be divided into very small regions of equal volume and that the magnesium atoms are distributed uniformly throughout only one-third of these regions. The copper atoms

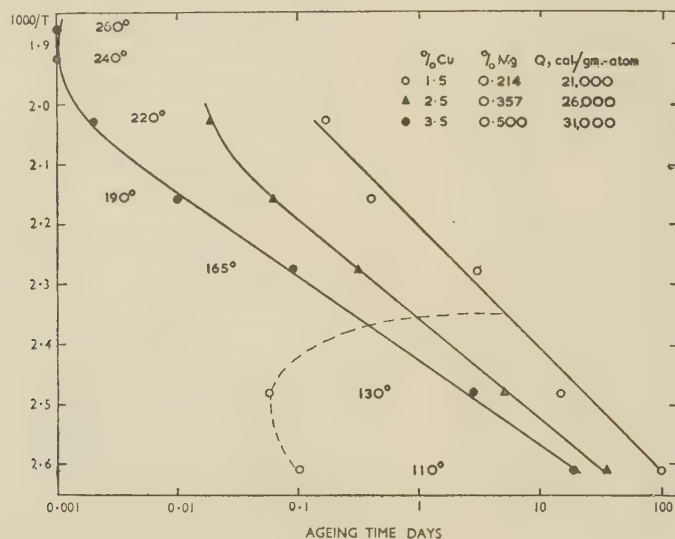


FIG. 10.—Incubation Values for the Rise-to-Peak-Hardness/Temperature Relationships for Alloys with a Copper : Magnesium Ratio of 7 : 1. Dotted line : suggested C curve for earlier incubation values.

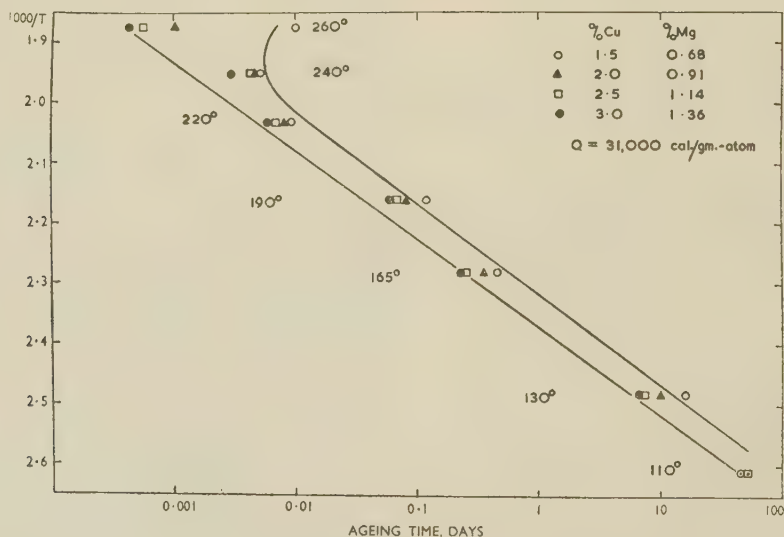


FIG. 11.—Incubation Values for the Rise-to-Peak-Hardness/Temperature Relationships for Alloys with a Copper : Magnesium Ratio of 2.2 : 1.

tated. Approximately five-eighths* of the copper out of solution is in the CuAl_2 and three-eighths* in Al_2CuMg . It is of interest to determine whether any part of the ageing curves for this series can be obtained by a simple mixture of the results on the binary

are assumed to be uniformly distributed throughout all the regions. The two-thirds of the regions free from magnesium are considered to age as binary aluminium-copper alloys, while the third containing both magnesium and copper ages as the pseudo-

* These may be regarded as two-thirds and one-third, respectively when the 2.2 : 1 series is taken as representing

the pseudo-binary alloys in place of the 2.61 : 1 wt. ratio in Al_2CuMg .

binary aluminium-S phase alloys, with a copper : magnesium weight ratio of 2 : 2 : 1.

The hardness increment during ageing for copper levels of 2.0, 2.5, and 3.0% was obtained by interpolation amongst the ageing curves of the 7 : 1 series of alloys. Two-thirds of the increment of the binary aluminium-copper alloys^{5,6} and one-third of the

flat plateau. The summed curves predict a lengthy flat at low or medium hardness increments, followed by a rapid rise either to peak hardness or to a plateau of short duration. However, the peak hardness times at 130° C. were in reasonable agreement.

The agreement was fairly good in the alloys with 2% copper aged at 165° C., but was less satisfactory

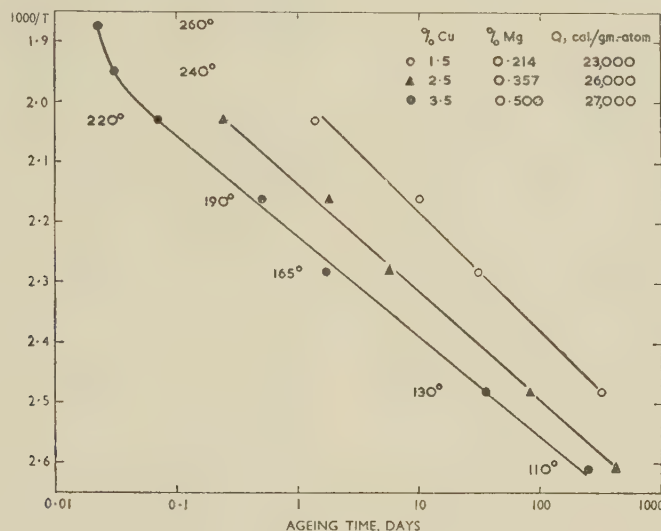


FIG. 12.—Time-to-Peak-Hardness/Temperature Relationships for Alloys with a Copper : Magnesium Ratio of 7 : 1.

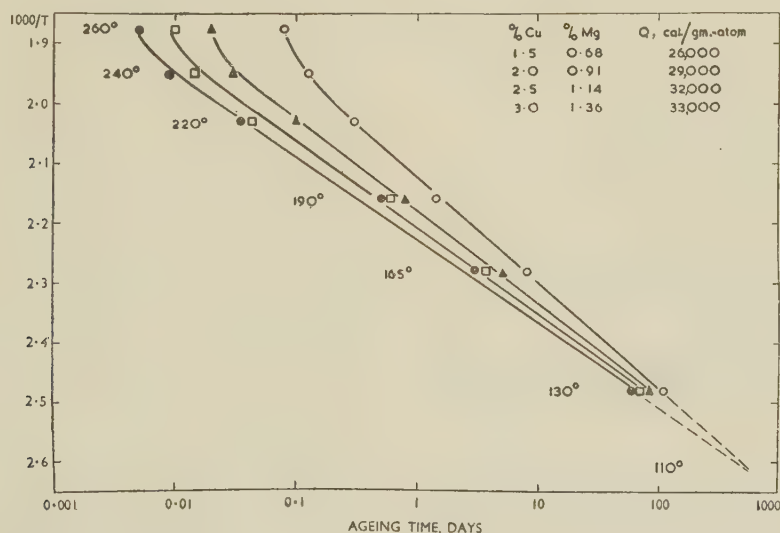


FIG. 13.—Time-to-Peak Hardness/Temperature Relationships for Alloys with a Copper : Magnesium Ratio of 2 : 2 : 1.

increment of the ternary alloys with a copper : magnesium ratio of 2 : 2 : 1, both at the same copper levels, were plotted and summed. The summed and experimental curves were only rarely in agreement as is shown by the results in Fig. 14 for the 3% copper alloys.

The chief difference at low ageing temperatures (110° and 130° C.) is that the experimental curves for the 7 : 1 series of alloys show a lengthy rise to their

at the higher copper contents. The peak-hardness times were again not dissimilar.

A three-stage ageing curve was predicted at 190° C. at the 2% copper level. Good agreement was found for the alloys with 2.5% copper. The 3% copper alloy gave a higher peak hardness, which also occurred earlier than in the summed curve. Complex inflected ageing curves were predicted at 220° C. which did not agree with the experimental curves.

It is quite clear that the early parts of the ageing curves at 110° and 130° C. (and at 165° C. in the 3% copper alloys) cannot be obtained by a simple mixture in any proportion of the curves, at constant copper levels, from the binary aluminium-copper and pseudo-binary aluminium-*S* phase alloys. On the

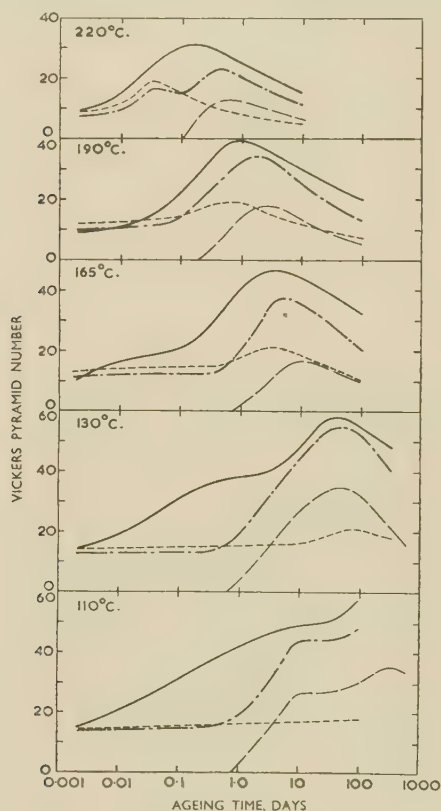


Fig. 14.—Hardness-Increment/Ageing Curves for Alloys with 3% Copper.

KEY.

- Experimental for alloys with a Cu : Mg ratio of 7 : 1.
- - - Two-thirds of increment for binary Al-Cu alloys.
- · - One-third of increment for alloys with a Cu : Mg ratio of 2.2 : 1.
- Summation of increments from the binary Al-Cu alloys and alloys with a Cu : Mg ratio of 2.2 : 1.

other hand, the agreement was good in the 2% copper alloys at 165° C. and in the 2.5% and 3.0% copper alloys at 190° C.

A slightly improved alternative assumption is that in a 7 : 1 alloy with $x\%$ copper, 57% of the regions contain 1.12 $x\%$ copper and no magnesium, whilst the remaining 43% contain all the magnesium and 0.84 $x\%$ copper. The compositions are parallel to the tie line from CuAl_2 to Al_2CuMg , but the synthesis of the ageing curves again proved equally unsuccessful.

V.—DISCUSSION

Silcock, Heal, and Hardy found a good correlation between the shape of the ageing curves and the precipitates present in binary aluminium-copper alloys.⁷ It seems likely that the same principle will apply to aluminium-copper-magnesium alloys,

although the absence of detailed X-ray work makes it difficult to interpret the ageing curves in terms of the various decomposition products.

The first stage of ageing in binary aluminium-copper alloys is due to the formation of disordered copper-rich regions, G.P. zones [1, Cu], on {100} planes of the matrix.^{3, 4, 7} The first stage of ageing in the pseudo-binary aluminium-*S* phase alloys is similarly due to aggregates of copper and magnesium atoms on {100} planes of the matrix;^{92, 93} these will be termed G.P. zones [1, *S*]. It is necessary to consider whether the parts of the ageing curve up to the final rise to peak hardness in the alloys with a copper : magnesium ratio of 7 : 1 are due to a mixture of zones [1, Cu] and [1, *S*] or due to an uninterrupted series of solutions, zones [1, Cu, Mg], between zones [1, Cu] and [1, *S*].

The solubility curves, Fig. 9 (p. 29), for the occurrence of decomposition products responsible for the flat plateaux are clearly of basic importance in assessing the ageing behaviour. Even if the tie-lines are not parallel to the 7 : 1 or 2.2 : 1 compositions they must originate at the solubility curves. It has been established (Fig. 14) that the early part of the ageing curves of the 7 : 1 series cannot be synthesized from mixtures of the curves for the binary copper and pseudo-binary *S* phase alloys. The dilatometric results of Fink, Smith, and Willey⁴⁹ on aluminium-copper-magnesium alloys at 30° C. reinforce this observation, since it is impossible to obtain the curves for the alloys of intermediate magnesium content by mixing the results on the binary 4% copper and ternary 4% copper-1.5% magnesium alloys.

Possible phase relationships are set out in Fig. 15, in which the metastable solubility curves have been obtained from Fig. 9. In Fig. 15 (a) the apex of the (α + [1, Cu] + [1, *S*]) phase field has been placed close to the equiatomic ratio to mirror the behaviour of the alloys in full equilibrium. This hypothesis is clearly wrong, because the α /(α + [1, Cu]) boundary has a most improbable form and would require that additions of magnesium sharply decreased the stability of the α solid solution. The apex of the (α + [1, Cu] + [1, *S*]) phase field has been placed at the solubility limit in binary copper alloys in Fig. 15 (b) and (c). The 7 : 1 series of alloys will then form [1, *S*] zones at 165° C. The more highly alloyed materials enter the (α + [1, Cu] + [1, *S*]) phase field at lower ageing temperatures (Fig. 15 (c)), which could account for the extra initial stage in the ageing curves (Figs. 2 and 4). An alternative suggestion is made in Fig. 15 (d), where the α solid solution is taken to be in metastable equilibrium with a series of zones [1, Cu, Mg] of variable composition.

It is not possible to decide between Fig. 15 (b) and (c) and Fig. 15 (d). The former do not overcome the difficulty that the curves for the 7 : 1 series in the (α + [1, Cu] + [1, *S*]) field could not be synthesized even approximately from the ageing behaviour of the binary copper and pseudo-binary *S* phase alloys. If Fig. 15 (d) be correct, it becomes necessary to assume that the initial rise of the three-stage curves

in some of the 7 : 1 series of alloys is due to the rapid formation (during heating) of zones containing more than the average magnesium content. This seems not unlikely, since a similar effect can easily be postulated for the 2·2 : 1 series, where the hardening during heating might be followed by a flat at shorter ageing times than were investigated. The distinction between two- and three-stage ageing curves then becomes almost meaningless, because the flat at very short ageing times may depend on the rate of heating and be accentuated by the logarithmic time scale.

The solubility curves in Fig. 15 approach the binary aluminium-copper side at a very shallow angle. Consequently, a small amount of magnesium markedly increases the supersaturation with respect to the

provide an opportunity for the formation of the other precipitate. An alternative explanation is that G.P. zones [2, Cu, Mg] are responsible for the rise to peak hardness and are then replaced by θ' and S' or S .

It is quite clear from the ageing curves why full reversion cannot be anticipated from highly alloyed materials with a copper : magnesium ratio of 2·2 : 1. The flat plateau which occurs at all temperatures up to 240° C. may be expected to limit the fall from the hardness after ageing at room temperature. At 260° C., the flat is absent or negligible but the rise to peak hardness starts so rapidly that it would interfere with reversion to the quenched hardness.

The ageing and solubility curves suggest that the alloys with a copper : magnesium ratio of 7 : 1 would be reversible between 220° and 260° C. The flat was almost absent at the lower temperature and the rise in hardness took longer than in the alloys containing more magnesium. The metastable solubility curve in Fig. 9 is higher than for the binary aluminium-copper alloys, so that the conditions for reversion would be more critical.

The ageing curves of the ternary aluminium-copper-magnesium alloys are in agreement with and can account for most of the effects observed by more limited work on alloys falling within the same compositional range.

ACKNOWLEDGEMENTS

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REFERENCES

1. A. Wilm, *Metallurgie*, 1911, **8**, 223 (translation *Metal Progress*, 1939, **36**, 259); *Aluminium*, 1936, **18**, 366.
2. M. L. V. Gayler and R. Parkhouse, *J. Inst. Metals*, 1940, **66**, 67.
3. A. Guinier, *J. Phys. Radium*, 1941, [viii], **3**, 124.
4. A. Guinier, *Acta Cryst.*, 1952, **5**, 121.
5. H. K. Hardy, *J. Inst. Metals*, 1951, **79**, 321.
6. H. K. Hardy, *ibid.*, 1953-54, **82**, (6), 236.
7. J. M. Silcock, T. J. Heal, and H. K. Hardy, *ibid.*, 1953-54, **82**, (6), 239.
8. N. S. Brommelle and H. W. L. Phillips, *ibid.*, 1948-49, **75**, 529.
9. A. T. Little, W. Hume-Rothery, and G. V. Raynor, *ibid.*, 1944, **70**, 491.
10. D. J. Strawbridge, W. Hume-Rothery, and A. T. Little, *ibid.*, 1948, **74**, 191.
11. W. Hume-Rothery, *Phil. Mag.*, 1936, [vii], **22**, 1013.
12. H. K. Hardy, *J. Inst. Metals*, 1952-53, **81**, 432.
13. H. Nishimura, *Nippon Kinzoku Gakkai-Si*, 1937, **1**, 8.
14. V. G. Kuznetsov and L. N. Guseva, *Izvest. Akad. Nauk. S.S.S.R.*, 1940, [Khim.], (6), 905.
15. D. A. Petrov and G. S. Berg, *Zhur. Fiz. Khim.*, 1946, **20**, 1475.
16. H. J. Axon and W. Hume-Rothery, *Proc. Roy. Soc.*, 1948, [A], **193**, 1.
17. E. R. Jette, G. Phragmén, and A. F. Westgren, *J. Inst. Metals*, 1924, **31**, 193.
18. J. B. Friauf, *J. Amer. Chem. Soc.*, 1927, **49**, 3107.
19. A. J. Bradley and P. Jones, *J. Inst. Metals*, 1933, **51**, 131.
20. I. Obinata and K. Mutuzaki, *Nippon Kinzoku Gakkai-Si*, 1941, **5**, 121.

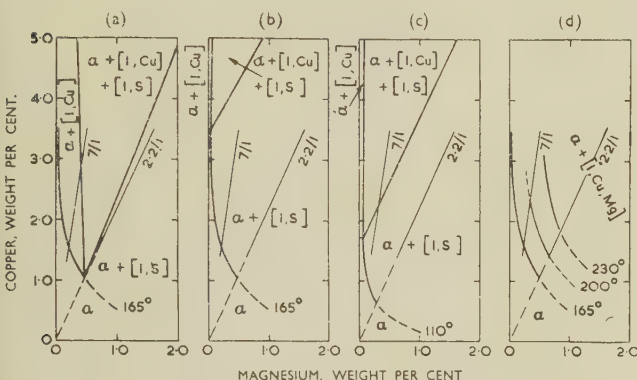


Fig. 15.—Hypothetical Phase Relationships for the Metastable Decomposition Products Giving Flat Plateaux.

- (a) Based on the solubility curves of Fig. 9 (p. 29) and the equilibrium diagram.
- (b) and (c) G.P. zones [1, Cu] and [1, S] assumed to be quite distinct.
- (d) G.P. zones [1, Cu, Mg] assumed to form an uninterrupted series of solutions between [1, Cu] and [1, S].

decomposition product, causing the hardness rise to the flat plateau. This adequately explains the observation that small quantities of magnesium accentuate and accelerate the ageing of aluminium-copper alloys at room and slightly elevated temperatures.

The final rise to peak hardness and softening was equally continuous in the alloys from both the 7 : 1 and 2·2 : 1 series. According to Bagaryatsky,^{92, 93} the peak hardness in the pseudo-binary aluminium-S phase alloys is due to the formation of the S' phase, and over-ageing is associated with loss of coherency of the more heavily strained orientation. His observation of sharp S' reflections after 30 min. at 218° C. was close to the peak of the ageing curve at 220° C. (Fig. 5).

The rise from the flat plateau to the peak in the alloys with 7 : 1 copper : magnesium may involve the G.P. zones [2] of the binary copper alloys, as well as the decomposition product of the pseudo-binary aluminium-S phase materials. When either of these has been formed, the unchanged G.P. zones [1, Cu] and [1, S] or [1, Cu, Mg] will be forced to redissolve, and this will probably

21. H. Perlitz and A. Westgren, *Arkiv Kemi, Min. Geol.*, 1943, [B], **16**, (13).
22. E. H. Dix, Jr., G. F. Sager, and B. P. Sager, *Trans. Amer. Inst. Min. Met. Eng., Inst. Metals Div.*, **1932**, 119.
23. H. Töllner, *Aluminium Archiv*, 1940, (34).
24. A. Schröder, *Metall*, 1949, **3**, 111, 150.
25. G. Phragmén, *J. Inst. Metals*, 1950, **77**, 489.
26. H. J. Axon, *ibid.*, 1952-53, **81**, 209.
27. H. J. Axon, *ibid.*, 1952-53, **81**, 449.
28. D. A. Petrov, *Acta Physicochim. U.R.S.S.*, 1937, **6**, 505.
29. M. L. V. Gayler and G. D. Preston, *J. Inst. Metals*, 1929, **41**, 191.
30. M. L. V. Gayler and G. D. Preston, *ibid.*, 1932, **48**, 197.
31. E. Schmid and G. Wassermann, *Metallwirtschaft*, 1928, **7**, 1329.
32. K. L. Meissner, *Z. Metallkunde*, 1929, **21**, 328.
33. H. Nishimura, *Nippon Kinzoku Gakkai-Si*, 1937, **1**, 59.
34. H. Nishimura, *ibid.*, 1937, **1**, 262.
35. D. A. Petrov, *J. Inst. Metals*, 1938, **62**, 63.
36. D. A. Petrov, *ibid.*, 1938, **62**, 81.
37. M. Hansen and K. L. Dreyer, *Z. Metallkunde*, 1938, **30**, 55.
38. M. Hansen and K. L. Dreyer, *ibid.*, 1939, **31**, 204.
39. M. Hansen and K. L. Dreyer, *Aluminium*, 1940, **22**, 134.
40. K. L. Dreyer and M. Hansen, *Z. Metallkunde*, 1943, **35**, 137.
41. K. L. Dreyer and M. Hansen, *Luftfahrtforsch.*, 1943, **20**, 323.
42. Y. Bresson, *Rev. Aluminium*, 1946, (128), 384.
43. K. L. Dreyer, *Metall*, 1947, **1**, 3.
44. A. S. Sharma, *Trans. Indian Inst. Metals*, 1948-49, **1**, (1), 39; (2), 11; 1949, **3**, 279.
45. W. Fraenkel and E. Scheuer, *Z. Metallkunde*, 1922, **14**, 49.
46. W. Fraenkel and E. Scheuer, *Naturwiss.*, 1924, **12**, 145.
47. I. Igarashi, *Sci. Rep. Tohoku Imp. Univ.*, 1924, [i], **12**, 333.
48. A. Eucken and H. Warrentrup, *Z. Elektrochem.*, 1935, **41**, 331.
49. W. L. Fink, D. W. Smith, and L. A. Willey, *Age-Hardening of Metals (Amer. Soc. Metals)*, **1940**, 31.
50. F. C. Althof, *Z. Metallkunde*, 1949, **40**, 54.
51. A. von Zeerleder and M. Bosshard, *ibid.*, 1927, **19**, 459.
52. L. W. Kempf and W. A. Dean, *J. Inst. Metals*, 1932, **48**, 213 (discussion).
53. K. L. Meissner, *ibid.*, 1930, **44**, 207.
54. K. L. Meissner, *ibid.*, 1931, **45**, 187.
55. P. Brenner and H. Kostron, *Z. Metallkunde*, 1937, **29**, 374.
56. M. Cohen, *Trans. Amer. Inst. Min. Met. Eng.*, 1939, **133**, 95.
57. R. W. Lindsay and J. T. Norton, *ibid.*, 1939, **133**, 111.
58. H. Borchers and O. Castellani, *Z. Metallkunde*, 1943, **35**, 128.
59. P. Laurent and H. Jarlan, *Rev. Mét.*, 1951, **48**, 759.
60. K. R. Jackman, *Aviation*, 1943, **42**, (8), 154; (9), 168; (10), 156.
61. B. Mitchell, *J. Aeronaut. Sci.*, 1943, **10**, (3), 86.
62. P. P. Mozley, *ibid.*, 1943, **10**, (6), 180.
63. M. E. Tatman and R. A. Miller, *Iron Age*, 1944, **153**, (4), 50.
64. T. L. Fritzlen and L. F. Mondolfo, *Metals and Alloys*, 1944, **20**, (4), 926.
65. T. L. Fritzlen and L. F. Mondolfo, *Metal Progress*, 1945, **45**, 1128.
66. H. Kästner, *Z. Metallkunde*, 1944, **36**, 1.
67. K. Gunn, *J. Roy. Aeronaut. Soc.*, 1950, **54**, 400.
68. W. D. Robertson, *Trans. Amer. Inst. Min. Met. Eng.*, 1946, **166**, 216.
69. H. L. Logan, H. Hessing, and H. E. Francis, *J. Research Nat. Bur. Stand.*, 1947, **38**, 465.
70. M. L. V. Gayler, *J. Inst. Metals*, 1922, **28**, 213.
71. M. L. V. Gayler, *ibid.*, 1923, **29**, 507.
72. M. L. V. Gayler, *ibid.*, 1923, **30**, 139.
73. P. L. Teed, "Duralumin and Its Heat-Treatment", p. 87. **1937**: London (Charles Griffin).
74. K. L. Dreyer, *Z. Metallkunde*, 1939, **31**, 147.
75. K. L. Dreyer, *Metallwirtschaft*, 1940, **19**, 843.
76. K. L. Dreyer, *ibid.*, 1943, **22**, 43.
77. K. L. Dreyer, *Metallforschung*, 1947, **2**, 362.
78. P. W. Boone, *Aircraft Eng.*, 1949, **21**, 56.
79. H. Nishimura, *Nippon Kinzoku Gakkai-Si*, 1938, **2**, 557.
80. W. O. Kroenig, *Z. Metallkunde*, 1931, **23**, 245.
81. W. Koch and F. W. Nothing, *Aluminium*, 1935, **17**, 535.
82. M. L. V. Gayler, *J. Inst. Metals*, 1937, **60**, 75.
83. H. Y. Hunsicker, *Age-Hardening of Metals (Amer. Soc. Metals)*, **1940**, 56.
84. A. Saulnier, *Rev. Aluminium*, 1949, (157), 235.
85. M. L. V. Gayler, *Proc. Roy. Soc.*, 1939, [A], **173**, 83.
86. F. Keller and A. H. Geisler, *Trans. Amer. Inst. Min. Met. Eng.*, 1944, **156**, 82.
87. A. H. Geisler and F. H. Keller, *ibid.*, 1947, **171**, 192.
88. F. Keller, *Inst. Metals Monograph and Rep. Series*, No. **8**, 1950, 85.
89. H. Nishimura and Y. Murakami, *Mem. Fac. Eng. Kyoto Univ.*, 1951, **12**, 47.
90. H. Nishimura and Y. Murakami, *ibid.*, 1953, **15**, 9.
91. H. K. Hardy and T. J. Heal, "Progress in Metal Physics", Vol. V, p. 143. **1954**: London (Pergamon Press).
92. Yu. A. Bagaryatsky, *Zhur. Tekhn. Fiz.*, 1948, **18**, 827 (Fulmer Research Inst. Translation No. 12).
93. Yu. A. Bagaryatsky, *ibid.*, 1950, **20**, 424 (Fulmer Research Inst. Translation No. 11).
94. H. Lambot, *Rev. Mét.*, 1950, **47**, 709.
95. H. Lambot, *Mem. Acad. Roy. Belg., Classe Sci.*, 1950, **26**, (1609).
96. H. K. Hardy, *J. Inst. Metals*, 1951-52, **80**, 483.

A HIGH-RESOLUTION EVAPORATED-CARBON REPLICA TECHNIQUE FOR THE ELECTRON MICROSCOPE *

1561

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SYNOPSIS

A simple two-stage replica technique, using an intermediate dry-stripped Formvar film and evaporated carbon as the final replica, is described. The carbon film, though very thin, is much more easily seen during the preparation than an equivalent silica film; largely because of this, the preparation time is short and results are consistent. The final resolution is better than 50 Å.

It is demonstrated that, contrary to previous belief, the Formvar film replicates the surface topography with a resolution of a few tens of Å. Even with very deeply etched specimens, results which are clear and easy to interpret are obtained.

I.—INTRODUCTION

THE successful application of the electron microscope to metallurgical problems has been hindered by the limitations of the replica methods used. Two basic types of replica are possible; these are illustrated in Fig. 1. The first (a) consists of a film following the



FIG. 1.—Basic Types of Electron-Microscope Replica.

contours of the specimen surface on one side and flat on the other; the second (b) is a film of uniform thickness with topography identical with the specimen surface. Typical of the first class is the Formvar replica,¹ which is most widely used. This is produced by applying a dilute solution of Formvar resin to the specimen and allowing the solvent to evaporate. The thin film formed is subsequently stripped from the surface. In practice, the top surface of the replica is not flat, but tends to some extent to follow the outline of the underlying structure. The second class is typified by the oxide² or silica³ replica. In the case of the silica replica, it is usual to take a preliminary casting of the surface with a thermoplastic material or by polymerizing a suitable monomer while it is in contact with the surface. After breaking off, silica or silicon monoxide⁴ is evaporated on to this first impression, and the film obtained separated by solution of the plastic.

The Formvar replica gives limited resolution, largely because it is relatively thick, and it proves a rather

unsuitable specimen from an optical point of view; hence it does not give a sharp image in the electron microscope. The oxide or silica replica is optically more suitable and results in higher-resolution images. However, the former is applicable only to certain metals, and the latter involves a relatively long and difficult preparation, mainly because the silica film is extremely difficult to see and to handle.

The two-stage replica method described in the present paper does not involve damaging the specimen, and is basically similar to the silica or silicon monoxide method, except that the thermoplastic material is replaced by Formvar and the silica by carbon. The production of single-stage replicas of specimens which can be dissolved away from the carbon film has been described elsewhere.⁵

II.—DESCRIPTION OF METHOD

Fig. 2 illustrates each stage in the production of a carbon replica, as described below:

(a) Coating with Formvar

The prepared specimen surface (e.g. as polished and etched) is first coated with a thin Formvar film, by flooding it with a 1–2% solution of Formvar in chloroform and then holding it vertically so that the excess solution drains on to a filter paper. After the remaining chloroform has evaporated, a film of resin is left on the surface.

(b) Backing with Bedacryl

For reasons which will appear later, it is necessary to back the Formvar with a separating layer, which also strengthens it. The backing film is formed by applying a 7% solution of Bedacryl 122X ‡ in benzene. The specimen is again drained vertically. After 2–3

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‡ Bedacryl 122X is an extremely soluble resin manufactured by I.C.I., Ltd. It is supplied as a 40% solution in xylene. This is diluted with benzene to 7% (wt./vol.) Bedacryl.

min. the backing film dries. It is important that the Bedacryl shall have thoroughly hardened before stripping is attempted; otherwise a form of strain structure may be introduced into the final replica. Hardening may be accelerated by gentle heating, e.g. under a 100-W. lamp. To facilitate dry-stripping,

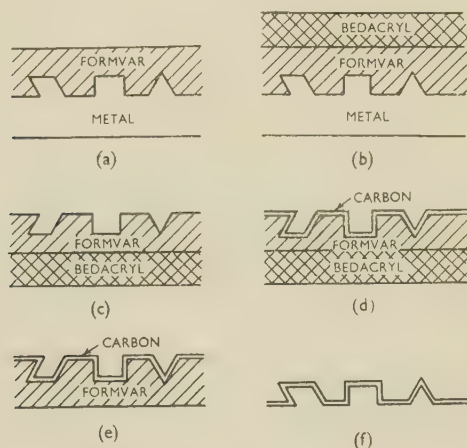


FIG. 2.—The Two-Stage Carbon-Replica Method.

- (a) Metal surface covered with layer of Formvar.
- (b) Metal surface covered with Formvar backed with Bedacryl.
- (c) Backed Formvar replica after dry-stripping.
- (d) Backed Formvar with carbon layer.
- (e) Formvar-carbon replica after removal of backing.
- (f) Final carbon replica after removal of first cast.

it is also desirable to score through the composite film round the edges of the specimen with a needle or a razor blade.

(c) Stripping of Replica

To remove the replica from the metal surface, a length of Sellotape is pressed firmly on to the Bedacryl. When the tape is stripped off, the backed Formvar film is removed with it. It is desirable to breathe heavily on the composite film before applying the Sellotape and to apply the latter before condensation from the breath has evaporated. This practice has been generally adopted with the dry-stripped Formvar-replica method and greatly assists in the removal of the replica, though the reasons for its effect are uncertain.

(d) Depositing Carbon Film

The carbon film is deposited by evaporating the carbon⁶ at normal incidence on to the Formvar. This process is carried out in a vacuum chamber by passing 20–30 amp. through two 5-mm.-dia. pointed carbon rods, the points of which are kept lightly pressed together. The rods should be of a hard graphitic carbon at least 99% pure. The desired current is obtained from a transformer rated at 12–20 V. and 20 amp. On passing the current, intense local heating occurs at the points and the carbon evaporates.

It is deposited as a brown film, easily visible on a piece of white glazed porcelain located about 8 cm. below the points. The Formvar-Sellotape assembly is placed beside the porcelain. To make the deposit still more easily visible, a drop of Apiezon "B" oil is put on the porcelain. The carbon cannot be seen on the area covered by the oil drop, which stands out in clear contrast against the darkening surround. A light-brown deposit, just detectable under these conditions, is obtained in approximately 1 sec. and is about 50 Å. in thickness.

A replica 50 Å. thick gives little contrast in the electron microscope without heavy-metal shadow-casting.⁷ If shadowing is not to be employed, a thickness of 200–300 Å. is required; this can be judged by a dark-brown colouring on the porcelain indicator. Good contrast now results, though there may be some loss in resolution.

(e) Removal of Bedacryl and Mounting of Replica

The method of removal of the Formvar-carbon combination from the Sellotape depends upon whether or not shadow-casting is to follow. If the replica is to be shadowed, it is clear that the shadowing material must be deposited on that surface of the carbon film which is in contact with the Formvar, for otherwise a negative impression of the specimen surface will be obtained from a photograph of the replica. Since shadowing cannot be satisfactorily carried out through the bars of a specimen grid, the carbon film must be mounted on the grid with the positive side * upwards. A simple mounting technique for use when it is not necessary to shadow the replica is described below (Method (i)). Two further methods leaving the film positive-side upwards are described in Methods (ii) and (iii).

Method (i).—After the deposition of the carbon, the strip of tape is removed from the vacuum apparatus and mounted on a glass microscope slide, with the replica facing outwards. It is then placed in a bath of acetone for about 2 min., after which the Bedacryl backing, in contact with the tape, has dissolved away and the acetone begins to affect the adhesive, turning it milky white. Since Formvar is insoluble in acetone, the Formvar-carbon combination remains intact. It does not float free, but is anchored to the Sellotape round the edges by the adhesive on the tape. It is now possible to tease up one edge of the film with a needle, and to insert a specimen grid between the Formvar and the tape, which is then removed from the solvent. Before the acetone evaporates, the grid is lifted, with a pair of fine-pointed forceps, about $\frac{1}{2}$ cm. from the tape without breaking the surrounding Formvar. It is held in this position while the acetone dries. The carbon-coated Formvar film is then cut away round the grid with a razor blade. This prevents the wet Formvar from curling under the grid and forming a double layer of carbon in the final replica. The grid is next bent slightly, with the film

* "Positive side" indicates that with topography identical with the metal specimen.

on the convex side, and placed, film upwards, on a $\frac{1}{8}$ -in. metal peg, in such a way that the grid is supported on the peg at the edges only; bending the grid prevents surface-tension effects from breaking the replica during the subsequent solution of the Formvar, which is described later. The carbon film is finally left with the positive side in contact with the grid.

Method (ii).—In the following two methods of mounting, the Formvar-carbon film is inverted, so that the final replica can be shadowed on the correct side. For the first method, a small tool is made by punching a $\frac{3}{16}$ -in. hole, $\frac{1}{16}$ in. from the end of a strip of thin copper sheet 3 in. long \times $\frac{3}{8}$ in. wide. The separation of the Formvar-carbon film from the Sellotape is carried out as before, by immersing the tape in an acetone bath. After the Bedacryl has dissolved, the ring-tool is slipped between the Formvar-carbon film and the tape. The combined film is then removed from the acetone and quickly inverted over a support grid, previously bent slightly and mounted, convex-side upwards, on a peg.

Method (iii).—The third method of mounting is very suitable for long narrow specimens, where the width of the replica is less than the diameter of the grid. Before immersing the Sellotape-Formvar-carbon assembly in the acetone, the Formvar-carbon-Bedacryl film is scored round its circumference with a razor blade. After immersing the tape in the acetone bath, a specimen grid is placed on the tape so that its edge just overlaps the edge of the Formvar-carbon film; this can now be folded back over the grid with a pair of fine-pointed forceps. The tape is lifted from the solvent bath in such a direction that the flow of liquid over the film does not disturb it from its position on the grid. The grid is now lifted $\frac{1}{2}$ cm. above the tape and the remainder of the mounting procedure carried out as in Method (i).

(f) Removal of Formvar

After mounting, the Formvar is removed from the carbon film by running 3 c.c. of chloroform over the grid at the rate of 1 c.c./min., from a burette so arranged that its nozzle is 2 mm. above the grid mounted on the peg. The removal of the grid from the peg by the initial contact of the chloroform is prevented by allowing one drop of acetone to fall upon the grid from a dropping pipette held about 3 cm. above it. After washing, the grid is dried under a lamp while still mounted on the peg. The replica is now ready for shadow-casting or examination in the electron microscope.

III.—EXAMPLES OF THE USE OF THE TECHNIQUE

The application of the replica technique described has demonstrated that, in addition to ease and speed of preparation, it gives micrographs of a resolution and clarity comparing very favourably with those obtained by any other method. There is little doubt

that this is because the Formvar follows the surface topography with great fidelity, and yet is sufficiently elastic to strip off without cracking or tearing, even when re-entrant cavities are encountered. The transference of the topographical detail to the carbon film provides a specimen optically suitable for good image formation and of great thermal and mechanical stability.

Fig. 3 (Plate V) shows a typical carbon replica from the deeply etched surface of a pearlitic steel (etched for $1\frac{1}{2}$ min. in 2% nitric acid in alcohol). In interpreting such a micrograph, it must be remembered that contrast results mainly from changes in film thickness in a direction parallel to the electron beam, due either to a change in slope of the film or to re-entrant areas giving a triple film thickness. An appreciation of the original structure can be achieved from such a micrograph, but heavy-metal shadowing leads to a contrast related to the original topography in a far more familiar manner. Fig. 4 (Plate V) is a micrograph of a shadowed replica of the same specimen as that in Fig. 3. As is usually the practice, the print is in the form of a negative, so that the appearance is that of a surface illuminated obliquely; the shadows produced throw the surface irregularities into sharp relief. The micrograph eliminates the difficulty in measuring the width : spacing ratio of the lamellae.⁸ It will also be noted that the ridge of each lamella is marked by an unexpected white band; this is the black band obtained in unshadowed pictures, reversed in the negative print. The effect can be minimized by keeping the carbon film thin.

Figs. 5 and 6 (Plate V) are micrographs of shadowed replicas from the surface of a copper-beryllium alloy, containing copper 97.5, beryllium 2, and cobalt 0.5%. The alloy was quenched from 830° C. and then age-hardened at 500° C. for 30 min. The specimen was polished mechanically and lightly electropolished in 67% phosphoric acid to clean up the surface; heavy etching was carried out in ammonium persulphate solution. The micrographs demonstrate the ability of the carbon replica to render an accurate and clear reproduction of a complex surface structure, and compare very favourably with micrographs of silica and Formvar replicas of similar copper-beryllium specimens published elsewhere.⁹

The resolution obtainable by the method can be estimated from Fig. 7 (a) (Plate VI), which is a micrograph ($\times 200,000$) of the sorbitic structure in an etched, tempered, carbon steel. The fine detail present suggests a potential resolution certainly better than 50 Å. The figure demonstrates that, contrary to previous belief, the Formvar has followed the surface detail with remarkable faithfulness. There is no indication that the molecular structure of the plastic limits the final resolution. It is therefore apparent that the one-stage Formvar replica is limited in its resolution, not because it fails to follow the surface topography accurately, but because it is not a suitable type of replica for use in the electron microscope. Fig. 7 (a) shows a pebble-like particle of

iron carbide protruding at an angle from the matrix. The manner in which the Formvar has stripped from the re-entrant space behind the pebble is clearly visible. A narrow white area, which appears as a band round the inside of each particle, is due to a self-shadowing property of evaporated carbon, whereby part of the carbon forms a uniform film over the whole specimen, while the remainder behaves like a shadowing metal. The shadows are visible because the source of carbon is not in the same alignment relative to the replica as the illuminating electron beam. This effect has also been observed in silica replicas.

The advantages of the carbon over the silica technique are mainly practical, though there appears to be some fundamental difference in the behaviour of the two substances when evaporated on to a surface.

The main practical benefit is that carbon replicas can be made easily and quickly. With a little practice, a replica can be prepared in less than 15 min. An important advantage lies in the high visibility of the carbon film, which can be seen without special lighting conditions throughout the preparation process. The replicas are very stable in the electron beam and, unlike those of the Formvar type, are eminently suitable for stereoscopy.

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REFERENCES

1. V. J. Schaefer and D. Harker, *J. Appl. Physics*, 1942, **13**, 427.
2. F. Keller and A. H. Geisler, *Trans. Amer. Inst. Min. Met. Eng.*, 1944, **156**, 82.
3. R. D. Heidenreich and V. G. Peck, *J. Appl. Physics*, 1943, **14**, 23.
4. G. Hass and N. W. Scott, *J. Opt. Soc. Amer.*, 1949, **179**, 39.
5. D. E. Bradley, *Brit. J. Appl. Physics*, 1954, **5**, 96.
6. D. E. Bradley, *ibid.*, 1954, **5**, 65.
7. R. C. Williams and R. W. G. Wyckoff, *J. Appl. Physics*, 1946, **17**, 23.
8. W. Hume-Rothery, *Inst. Metals Monograph and Rep. Series*, No. **8**, 1949, p. 148 (discussion).
9. D. Harker and M. S. Murphy, *Trans. Amer. Inst. Min. Met. Eng.*, 1945, **161**, 75.

THE FORMATION AND REMOVAL OF TWINS IN TITANIUM DURING DEFORMATION *

1562

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SYNOPSIS

It is shown that deformation twins produced in titanium single crystals by bending can be removed by unbending or annealing the crystal.

I.—INTRODUCTION

TWINNING during deformation has been reported ^{1,2} on the (11 $\bar{2}$ 1), (11 $\bar{2}$ 2), (11 $\bar{2}$ 3), and (11 $\bar{2}$ 4) planes in polycrystalline titanium, as well as on the (10 $\bar{1}$ 2) plane characteristic of all close-packed hexagonal metals. During the deformation of single crystals of van Arkel titanium produced by a modification of the strain-anneal technique,³ twinning was observed by the present author on (10 $\bar{1}$ 2) and (11 $\bar{2}$ 2) planes only. These crystals had a Vickers hardness No. of 90, which is equivalent to a combined oxygen and nitrogen content of 0.01%.⁴

Twins of the (10 $\bar{1}$ 2) type usually have a lenticular form rather than the lamellar form reported ² to be common to the lower-order twins. This is no doubt due to the lower shear involved in the formation of (10 $\bar{1}$ 2) twins.⁵ On annealing at 800° C., twins of this type are absorbed, with or without recrystallization.⁶

II.—FORMATION OF TWINS DURING TENSILE ELONGATION

(10 $\bar{1}$ 2) twins are formed during tensile testing of single crystals of certain orientations. The twins form initially as thin lamellae which spread with increasing deformation both in length and in breadth to take on a lenticular form. Although the formation of the initial lamellae appears to be very rapid, the expansion or growth of a twin takes place in a regular manner with increasing deformation. The bounding surface between a twin and the matrix seems to be readily movable, and under suitable stress conditions there appears to be no reason why detwinning should not take place.

III.—THE FORMATION AND REMOVAL OF TWINS DURING BEND TESTS

An electropolished crystal was subjected to various degrees of bending, such that the compressive and tensile stresses produced by bending acted along the axis of the specimen. In this manner the stresses could be easily reversed by bending in the opposite sense.

On a crystal 2 mm. thick, bent to a radius of 110 mm., (10 $\bar{1}$ 2) twins were observed, together with (10 $\bar{1}$ 1)-type slip, on the compression face at about 45° to the direction of the applied stress. The tension face showed only (10 $\bar{1}$ 1) slip. On further bending to a radius of 55 mm., the original twins thickened and lengthened. At this stage the specimen was flattened to its original shape, with the result that the twins very nearly disappeared (Fig. 1, Plate VII). Bending in the opposite sense failed to remove the last traces of the twins. On rebending in the original direction to a radius of 18 mm. (Fig. 2, Plate VII), the traces of the original twins again expanded and once again nearly disappeared on straightening the crystal (Fig. 3, Plate VIII). If the crystal was bent to even smaller radii, the large lenticular twins expanded until they met, leaving an apparently homogenous sheet of twin. On unbending after this stage had been reached, far more narrow lamellar twins remained than were present before bending, suggesting that the lamellar twin nuclei are not unique and can be increased in number by repeated twinning and detwinning. The original nuclei were, however, still preserved (see Figs. 2 and 3). Twins which formed in a neighbouring grain at a different inclination to the stress axis also disappeared on unbending.

The change in shape of the twins, during both expansion and contraction, took place by the simultaneous movement of the two boundaries of the twin. The rates of movement of the two boundaries and of the boundaries of neighbouring twins were not necessarily the same. Occasionally the movement of an individual boundary was momentarily halted until an increased local applied stress was built up, which enabled it to move forward again.

These observations were made on unetched, electropolished surfaces of the crystals. The twins were therefore visible under the microscope by virtue of the tilt produced at the surface by the shear involved in the twinning process. That mechanical detwinning involved an exact reversal of the twinning process was implied, as the tilt produced at the surface disappeared on detwinning. During thermal detwinning, however, the removal of the twins did not appear to take place

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by an exact reversal of the twinning process, as the tilt produced on the surface did not disappear during the thermal treatment (see Fig. 4, Plate VIII).

During bending and unbending the slip appeared to increase at each operation, although unslipping has been claimed in zinc by Washburn and Parker.⁷

IV.—DISCUSSION

Some observations on the mobility of twin boundaries have been reported for other metals. Deformation twins have been shown to grow on annealing α -uranium,⁸ α -iron,⁹ and zinc;¹³ on the other hand, they have also been shown to be absorbed by annealing without recrystallization in beryllium,¹⁰ bismuth,¹¹ NaNO_3 ,¹² zinc,¹³ and α -uranium.⁷ The mechanism of thermal detwinning would appear to be that of grain growth. Whether a thermal treatment resulted in a twin growing or being absorbed by the matrix would depend on the state of strain of the twinned region relative to that of the matrix. The formation of twins was in most cases accompanied by slip in the matrix. The amount of slip in the matrix relative to the size of twin formed, would be dependent on the particular orientation of the grain relative to the direction of the applied stress. Cases of absorption and growth of twins might both be expected to occur, therefore, depending upon the initial stress conditions.

There is evidence of mechanical detwinning in bismuth,¹¹ antimony,¹⁴ α -uranium,¹⁵ and zinc.¹⁶ In the case of bismuth, the twins were reported to grow at a stress some 20% below that necessary to initiate new

twins, which, in its turn, was lower than the reverse stress required to bring about detwinning.

A dislocation model of mechanical twinning has been proposed by Cottrell and Bilby,¹⁷ in which a perfect dislocation was considered to dissociate at a node into a sessile and a twinning dislocation. The Burgers vector of the twinning dislocation was such that under an applied stress the dislocation rotated about the sessile dislocation, climbing one atom plane with each revolution and producing the correct amount of twinning shear on each plane that it swept. The twinning dislocation trailed behind it a layer of stacking faults. The ratio of the area of the boundary between the stacking fault and the perfect lattice to the volume of a twin will be greatest for the initiation of a twin. The stress required to initiate a twin will, therefore, be greater than that for it to spread, which is in accord with certain experimental observations, such as the marked discontinuities observed in the stress/strain curve during twinning in α -iron¹⁸ and the sudden appearance of critical twin lamellae, as in titanium. The fact that twinning is a far less violent process in titanium than in iron suggests that the stacking faults produced have a much lower energy. The ease with which the boundary of the twin and matrix can be made to migrate suggests, by analogy with the stress-induced movement of certain types of grain boundaries,¹⁹ that this boundary consists of a simple dislocation array.

ACKNOWLEDGEMENTS

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REFERENCES

1. T. S. Liu and M. A. Steinberg, *J. Metals*, 1952, **4**, 1043.
2. F. D. Rosi, C. A. Dube, and B. H. Alexander, *Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197**, 257.
3. F. D. Rosi and F. C. Perkins, *Trans. Amer. Soc. Metals*, 1953, **45**, 972.
4. A. T. Churchman, *Nature*, 1953, **171**, 706.
5. A. T. Churchman, unpublished work.
6. E. O. Hall, *Acta Cryst.*, 1953, **6**, 570.
7. A. T. Churchman, *A.E.I. Research Rep.*, 1953, (A.310).
8. J. Washburn and E. R. Parker, "Modern Research Techniques in Physical Metallurgy", p. 186. 1953: Cleveland, O. (American Society for Metals).
9. R. W. Cahn, *Acta Met.*, 1953, **1**, 49.
10. L. B. Pfeil, *Carnegie Schol. Mem. Iron Steel Inst.*, 1926, **15**, 319.
11. H. H. Hausner and N. P. Pinto, *Trans. Amer. Soc. Metals*, 1951, **43**, 1052.
12. I. A. Gindin and V. I. Startsev, *Zhur. Eksper. Teoret. Fiziki*, 1950, **20**, 738.
13. R. I. Garber, *ibid.*, 1947, **17**, 63.
14. C. H. Mathewson and A. J. Phillips, *Trans. Amer. Inst. Min. Met. Eng., Inst. Metals Div.*, 1927, 143.
15. G. Wassermann, *Z. Krist.*, 1930, **75**, 369.
16. E. R. W. Jones and W. Munro, *J. Mechanics Physics Solids*, 1953, **1**, (3), 182.
17. D. C. Jillson, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, **188**, 1009.
18. A. H. Cottrell and B. A. Bilby, *Phil. Mag.*, 1951, [vii], 42, 573.
19. A. T. Churchman and A. H. Cottrell, *Nature*, 1951, **167**, 943.
20. C. H. Li, E. H. Edwards, J. Washburn, and E. R. Parker, *Acta Met.*, 1953, **1**, 223.

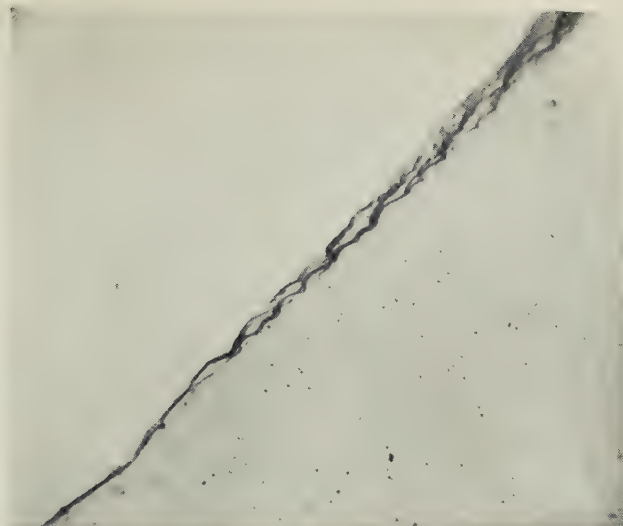


FIG. 7.—Serrated Grain Boundary in Aluminium-Copper Specimen No. 2; 4.5% Extension in 125 hr. at $\frac{3}{8}$ ton/in.². $\times 1000$.



FIGS. 8 and 9.—Appearance of Surface of Alloy and Pure Aluminium Specimens Extended Similar Amounts in Similar Times. $\times 50$.

FIG. 8.—Al-Mg specimen No. 3; 15.2% extension in 769 hr. at $\frac{3}{8}$ ton/in.².

FIG. 9.—Aluminium; 17% extension in 696 hr. at $\frac{1}{2}$ ton/in.².

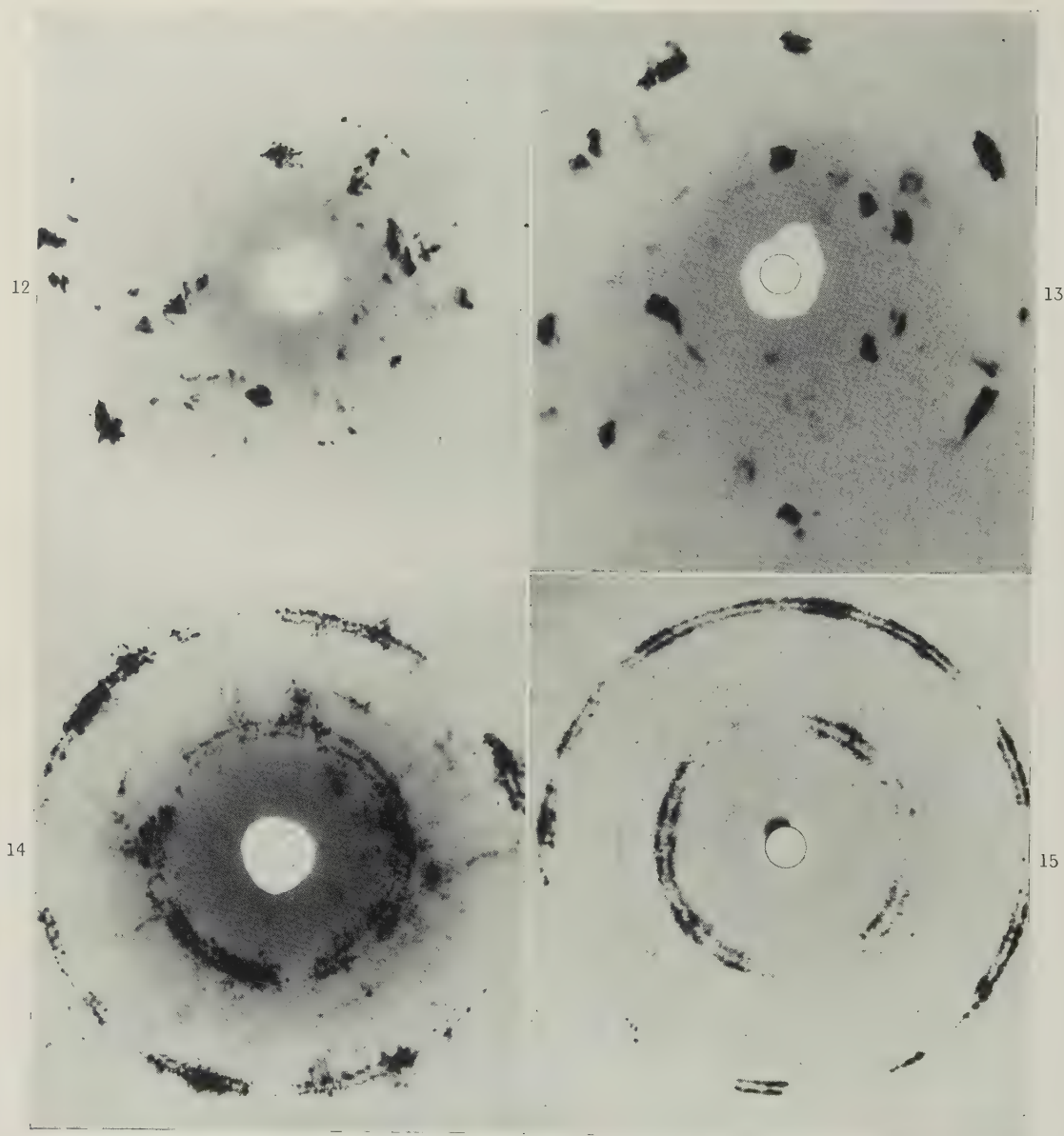
FIGS. 10 and 11.—Appearance of Surface of Alloy and Pure Aluminium Specimens Extended Similar Amounts Under the Same Stress. $\times 50$.

FIG. 10.—Al-Zn specimen No. 3; 5% extension in $48\frac{1}{2}$ hr. at $\frac{1}{2}$ ton/in.².

FIG. 11.—Aluminium; 7% extension in $118\frac{1}{2}$ hr. at $\frac{1}{2}$ ton/in.².

FIGS. 8-11 reduced by $\frac{1}{5}$ in reproduction.

[To face p. 10.]



FIGS. 12-15.—X-Ray Back-Reflection Patterns Obtained from Alloy and Pure Aluminium Specimens After Similar Extensions at a Given Stress but Different Times.

- FIG. 12.—Al-Cu specimen No. 4; 2.34% extension in $550\frac{1}{2}$ hr. at $\frac{1}{2}$ ton/in.².
 FIG. 13.—Aluminium; 2.1% extension in 5 hr. at $\frac{1}{2}$ ton/in.².
 FIG. 14.—Al-Mg specimen No. 3; 15.2% extension in $769\frac{1}{4}$ hr. at $\frac{3}{4}$ ton/in.².
 FIG. 15.—Aluminium; 15% extension in 25 hr. at $\frac{3}{4}$ ton/in.².

CRACKING OF D.T.D. 683 ALLOY.

← Torsion axis.

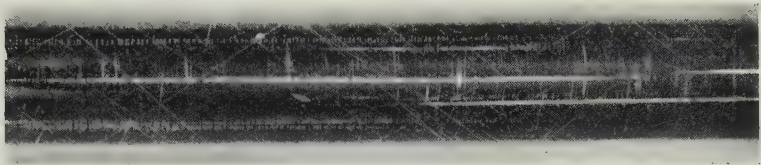


FIG. 5.—Bands of Short Circumferential Cracks Produced by Cyclic Torsional Stressing. $\times 7$.

← Torsion axis.

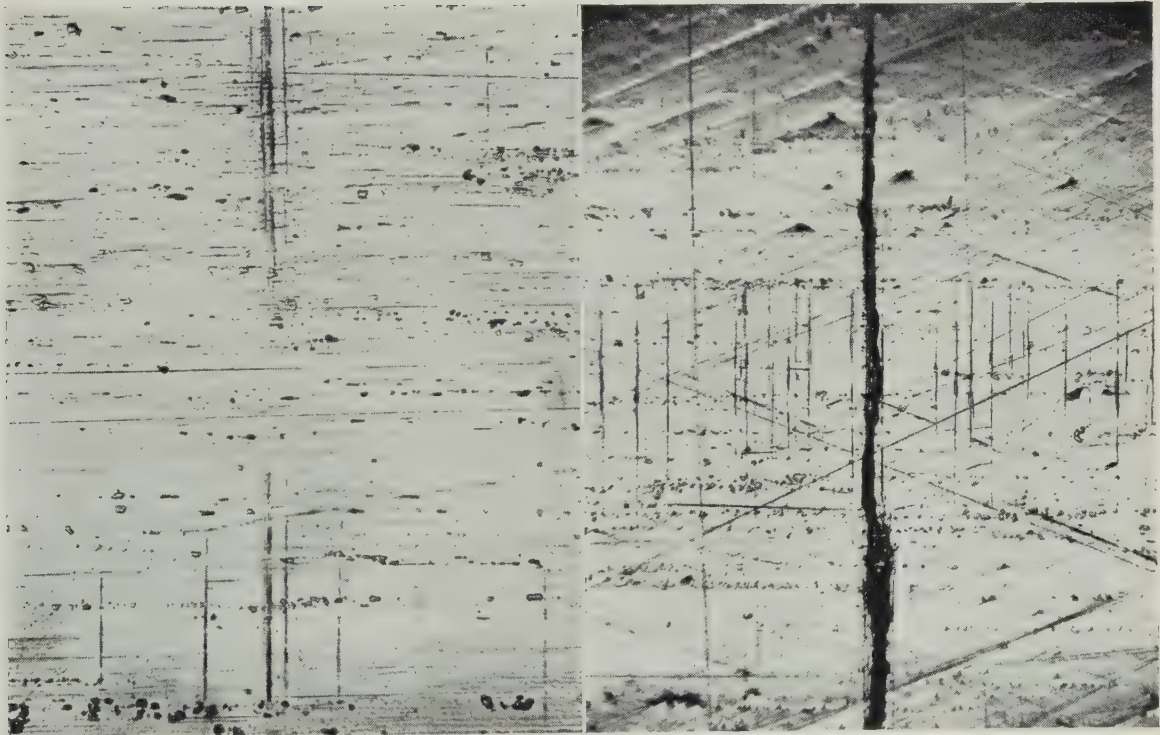


FIG. 6.—Late Stage in the Development of Short Circumferential Cracks by Cyclic Stressing. $\times 200$.

FIG. 7.—Major Torsional Fatigue Crack. $\times 200$.

Specimens as polished for fatigue testing.

MICROSTRUCTURES OF D.T.D. 683 ALLOY.

← Torsion axis.



FIG. 8.—Section Showing the Precipitated Regions and the Associated Short Crack Produced by Torsional Cyclic Stressing. $\times 1500$.

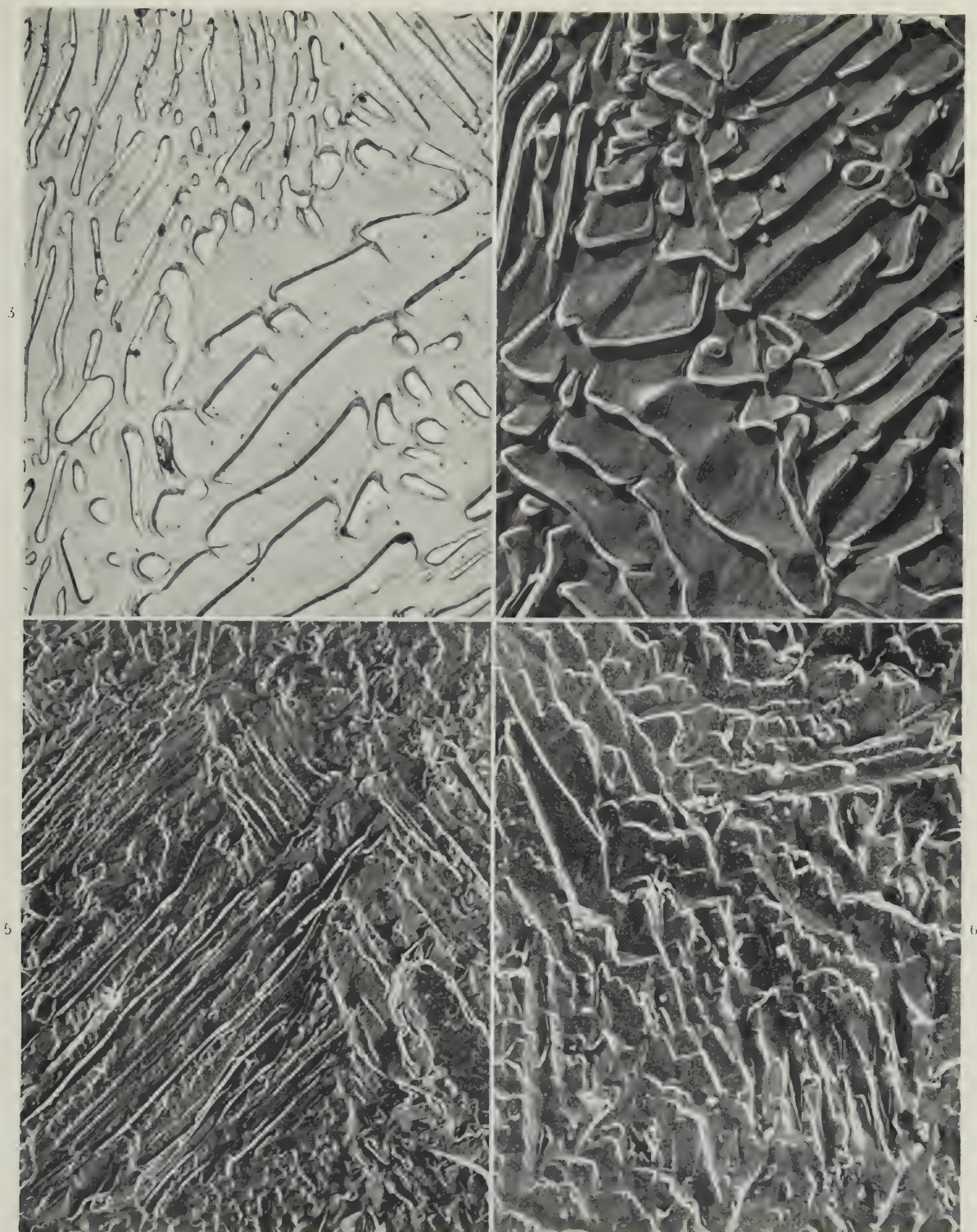
FIG. 9.—Sub-Surface Precipitation Bands Produced During Cyclic Stressing. $\times 500$.

FIG. 10.—Intermediate Stage of Precipitation by Cyclic Stressing. $\times 500$.

FIG. 11.—Early Stage of Precipitation by Cyclic Stressing. $\times 1500$.

All polished and etched with aqueous 25% HNO_3 .

ELECTRON MICROGRAPHS FROM CARBON REPLICAS.

FIG. 3.—Unshadowed Replica of a Coarse Pearlite Structure in Steel. $\times 7500$.FIG. 4.—Replica of Same Structure as in Fig. 3, Gold-Palladium Shadowed at 2 : 1. Negative print. $\times 10,000$.

FIGS. 5 and 6.—Replicas of Surface of Age-Hardened Copper-Beryllium Alloy, Gold-Palladium Shadowed at 3 : 1. Negative prints.

FIG. 5.— $\times 12,000$.FIG. 6.— $\times 18,000$.

ELECTRON MICROGRAPH FROM CARBON REPLICA.

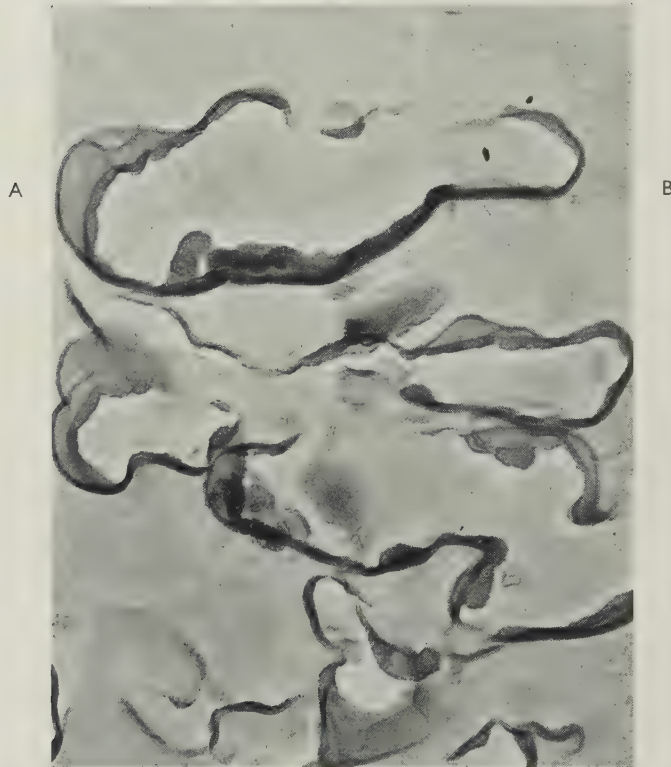


FIG. 7 (a).—Evaporated Carbon Replica of Sorbitic Structure in Etched Tempered Carbon Steel. Unshadowed. $\times 200,000$.

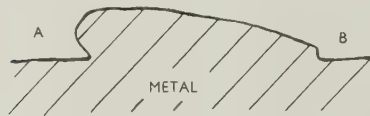


FIG. 7 (b).—Cross-Section of Iron Carbide Grain Shown in Fig. 7 (a), As Interpreted from Contrast Variations.

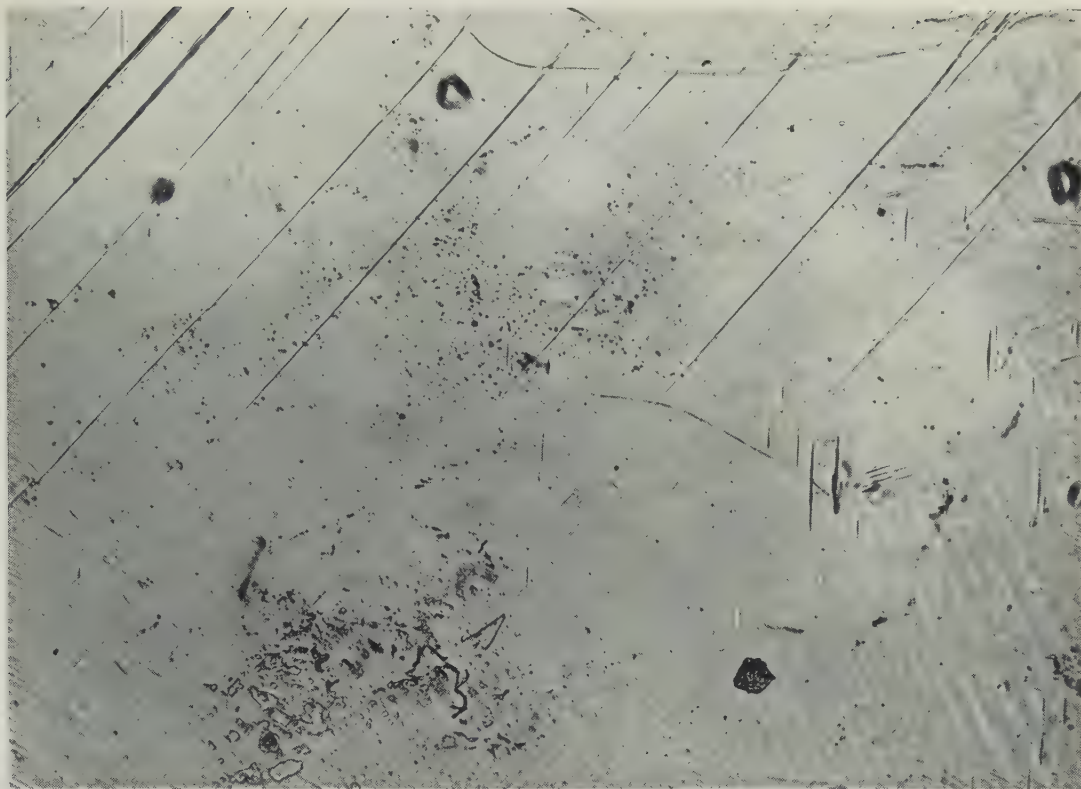


FIG. 1.—An Area of the Compression Face of an Electropolished, Unetched Bend Specimen. In a flattened condition after two previous bend tests. Note the narrow (1012) twin nuclei starting from the crystal boundary. $\times 200$.

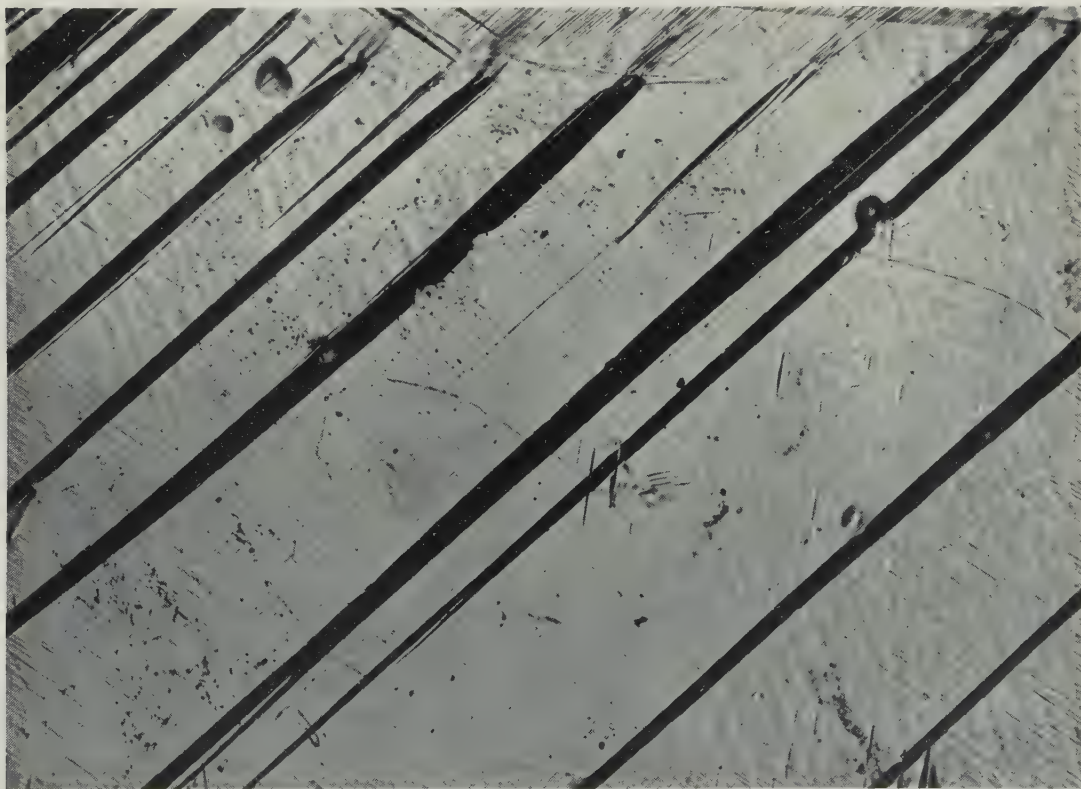


FIG. 2.—Same Area as in Fig. 1. After rebending; the nuclei have spread laterally and longitudinally. $\times 200$.
Both reduced by $\frac{1}{10}$ in reproduction.

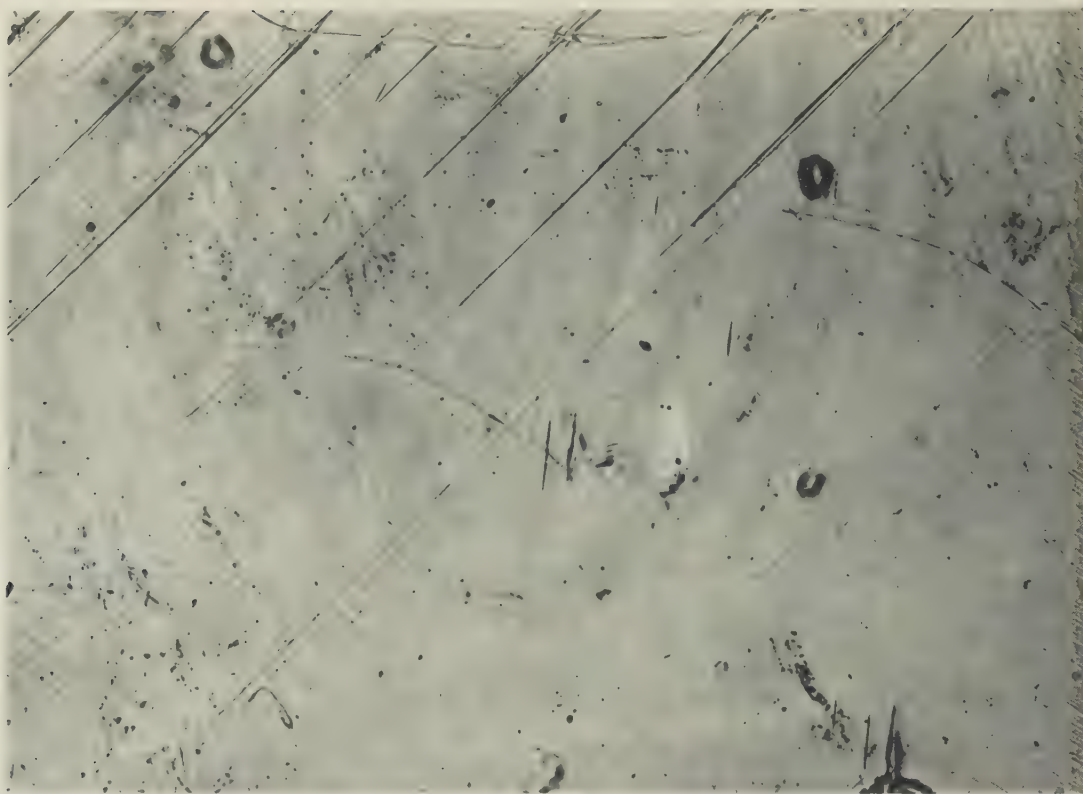


FIG. 3.—Same Area as in Figs. 1 and 2. After re-flattening the crystal; the twins have contracted again, leaving the original nuclei in the same positions as in Fig. 1. There has been some multiplication of existing nuclei. $\times 200$.

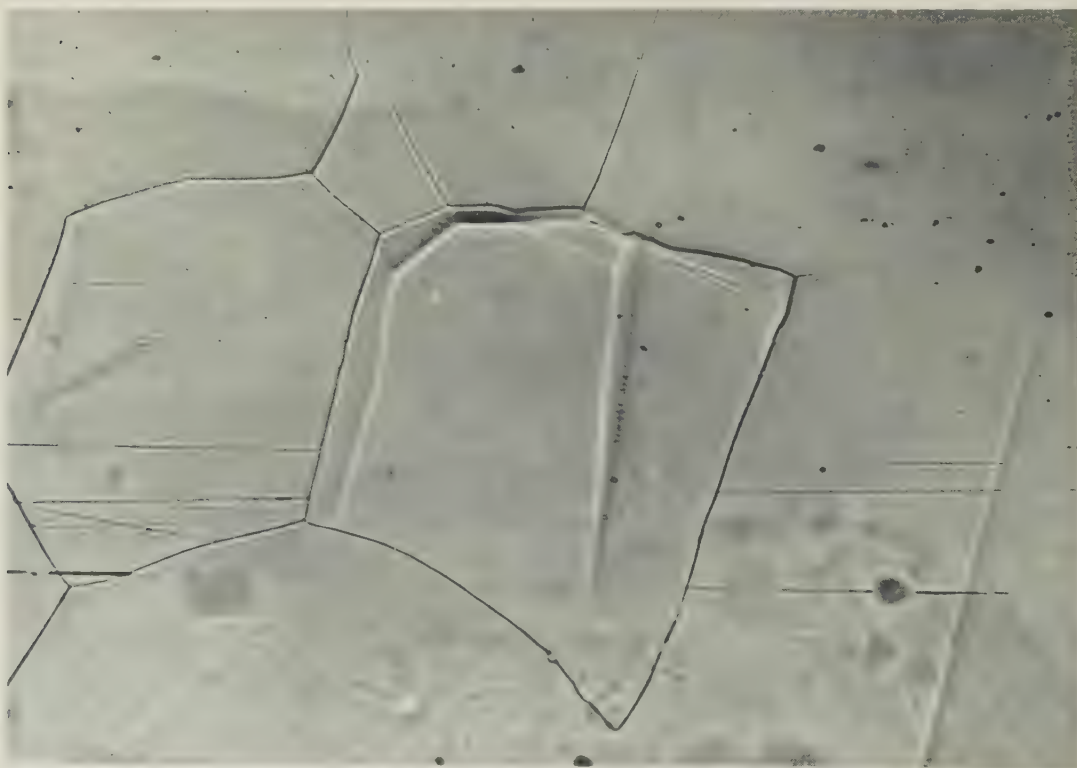


FIG. 4.—An Electropolished Specimen Which Was Deformed to Produce (1012) Twins and Then Annealed at 860°C . The surface has been lightly electropolished to round off the surface tilt which appeared during the formation of the twins. This tilt has not disappeared, although the twin has been absorbed during the annealing treatment. $\times 180$.

Both reduced by $\frac{1}{10}$ in reproduction.

INFLUENCE OF COLD DEFORMATION ON THE YOUNG'S MODULUS OF SOME NON-FERROUS METALS*

1563

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SYNOPSIS

Young's modulus values of copper, brass, and aluminium after increasing amounts of cold working, principally by rolling, have been determined and correlated with microstructural and X-ray observations, as well as with the results of earlier investigations.

As a result of cold rolling, the elastic modulus of copper decreases progressively at 45° to the rolling direction, while it increases in the transverse direction, and also in the rolling direction after an initial decrease. All the evidence suggests that the initial decrease in the direction of the principal axis of strain is associated with the generation of mobile lattice dislocations; and that the subsequent increase in modulus with greater amounts of deformation in the same direction and normal to it, as well as the progressive decrease at 45°, can be largely explained by the development of primary and secondary textures and the known anisotropy of the copper lattice.

The effect of cold working on the elastic modulus of brass, measured transversely and at 45° to the direction of rolling, is similar to that found with copper. In the direction of principal strain, however, the modulus, as in copper, decreases initially, but thereafter rises to a maximum and then decreases. The progressive increase and decrease in modulus transversely and at 45° to the rolling direction, respectively, are attributable to the development of preferred orientation, but the decrease in modulus in the rolling direction with reductions in excess of 20% is probably associated with the formation of structural discontinuities coarser in scale than lattice dislocations.

With super-pure aluminium, which is almost isotropic and where, therefore, there is no complication of preferred orientation, the modulus falls initially as the result of mobile lattice dislocations, and thereafter more gradually as a consequence of coarser structural discontinuities.

The observed effects of cold deformation on elastic modulus of the three materials examined are associated with lattice distortion, involving generation of mobile dislocations after small strains and coarser-scale structural discontinuities after larger strains, and also with the development of preferred crystalline orientation.

I.—INTRODUCTION

It is well known that when some metals are plastically deformed in the cold state, as in many industrial cold-working operations, a preferred crystal orientation is developed resulting not only in measurable, but often in quite considerable, differences in properties in different directions relative to that of the deformation. The amount of information regarding such differences in elastic modulus values is, however, very limited and, moreover, it is not known to what extent these differences are associated with (1) lattice distortion and work-hardening, or (2) preferred orientation and lattice anisotropy. With the object of obtaining more data and some clarification of this issue, a study has been made of the effect of deformation on the elastic modulus values of pure copper and of α -brass, which have a high degree of elastic anisotropy, and of super-pure aluminium, which is almost isotropic. A large number of modulus determinations

have been carried out on material deformed in a variety of ways and the results related to structural changes observed by microscopic and X-ray techniques, and to the results of earlier investigations.

II.—METHOD OF DETERMINING MODULUS VALUES

Young's modulus values of the various materials were determined using a Denison single-lever testing machine of 3000-lb. capacity and a Lamb roller extensometer of 1 in. gauge-length sensitive to increments of strain of about 1×10^{-6} , the specimens being held in Robertson ball-aligning shackles. Great care was taken to ensure that loading was axial, test-pieces being machined symmetrically to dimensions well within the usual tolerances, ± 0.001 in. In addition, holes were drilled in the shoulders of strip specimens with their centres located on the axis of the parallel portion of the gauge-length by means of a

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special jig. Furthermore, to eliminate possible errors arising from thermal expansion, testing of specimens was not begun until 1 hr. after assembly in the apparatus, thus allowing the system to attain a constant and uniform temperature. Loads were applied in equal increments to a maximum well within the known limits of proportionality, the procedure being repeated six times for each specimen. In several experiments the strain increments were measured on unloading as well as during loading, but no differences in slope of the load/extension line, nor therefore in modulus, were observed. The strain at the limit of proportionality of annealed aluminium is about 4×10^{-5} , and at that of annealed copper about 6×10^{-5} ; thus the error of a single modulus determination is $<3\%$ or $<2\%$, respectively, and for deformed and work-hardened material $<1\%$. The differences between the maximum and minimum values found in any series of six determinations were, in fact, all within these limits. The error in mean values from six determinations is, therefore, in general not greater than 1% .

III.—EFFECT OF DEFORMATION BY COLD ROLLING AND DRAWING

1. PREPARATION OF MATERIALS

From a slab and billet of standard commercial-quality H.C. copper of the composition indicated in Table I, strip and rod were produced for determining

TABLE I.—Composition of High-Conductivity Copper.

	Strip	Rod
	%	%
Copper	99.94	99.96
Oxygen	0.045	0.034
Tin	<0.0005	0.0002
Lead	0.0005	<0.0002
Iron	0.001	0.001
Nickel	0.0008	0.0005
Manganese	<0.0005	<0.0005
Silver	0.0025	0.0022
Antimony	0.0004	<0.0001
Bismuth	<0.0001	<0.0001
Arsenic	<0.0005	<0.0005
Phosphorus	0.0003	Nil

the effect of cold rolling and drawing, respectively, on the modulus. The strip was prepared by hot rolling a $3\frac{1}{2}$ in. thick cast slab to $1\frac{1}{2}$ in., and cutting transversely to 8 in. widths which were cold rolled at right angles to the hot-rolling direction to a thickness of 0.6 in. At this stage the strip was annealed for 1 hr. at 500°C . In this condition the crystal structure was random, with a uniform grain-size of about 0.025 mm., and the strip was cold rolled in a series of passes to nominal reductions in thickness of 5%, 10%, and at 10% intervals to 90%. Both before the cold rolling and at each reduction stage, duplicate tensile test-pieces, conforming to B.S. 485, were cut parallel, transverse, and at 45° to the rolling direction for modulus evaluation.

To provide material for the study of the influence of cold drawing, extruded rod at $1\frac{3}{8}$ in. dia. was annealed and cold rolled to 1 in. dia., drawn to $\frac{7}{8}$ in., and finally annealed for 1 hr. at 500°C . The grain-size at this stage was uniform at 0.03 mm., with evidence of a slight degree of preferred orientation of crystals with either a $\langle 111 \rangle$ or $\langle 100 \rangle$ axis parallel to the rod axis. This stock was cold drawn with nominal reductions in area of 5%, 10%, and at 10% intervals to 90%, and duplicate tensile test-pieces of 0.282 in. dia. conforming to B.S. 18 were prepared from rod samples in the annealed conditions and after each reduction.

Brass strip of the composition indicated in Table II,

TABLE II.—Composition of 70:30 Brass.

Copper	69.10%
Tin	Trace
Lead	$<0.01\%$
Iron	0.01%
Nickel	0.01%
Antimony	0.002%
Bismuth	$<0.0005\%$
Arsenic	$<0.003\%$
Silicon	Not detected
Phosphorus	Not detected
Zinc	Remainder

with random orientation of crystals and a uniform grain-size of 0.04 mm., was prepared by hot rolling a $3\frac{1}{2}$ in. slab to 1 in. and cutting it transversely to 8 in. widths, cold rolling these at right angles to the direction of hot rolling to 0.5 in. thick, annealing for 1 hr. at 550°C ., then further cold rolling to 0.3 in. and annealing as before. This stock was cold rolled in a series of passes with nominal reductions in thickness of 5% and 10%, and at 10% intervals to 90%. From strip in the annealed condition and after each reduction, duplicate tensile test-pieces to B.S. 485 were cut at 0° , 45° , and 90° to the rolling direction.

An 8 in. thick cast slab of super-pure aluminium of the composition indicated in Table III was hot rolled

TABLE III.—Composition of Super-Pure Aluminium.

Copper	0.0015%
Iron	0.0032%
Silicon	0.0034%
Magnesium	0.0019%
Aluminium	Remainder

to 2 in., cut transversely to 8 in. widths, further hot rolled in this transverse direction to 0.75 in., annealed at 450°C . for 4 hr., cold rolled to 0.3 in., and finally annealed for 24 hr., at 300°C . These processing conditions, which were established in the course of another investigation, resulted in a uniform structure of grain-size about 0.07 mm., with some slight degree of preferred orientation and directionality. The 0.3 in. strip was cold rolled, with reductions ranging from 5 to 90% and, except for strip rolled 90%, test-pieces were cut only at 0° to the rolling direction, since it is known that the degree of elastic anisotropy of aluminium is relatively slight.

2. EXPERIMENTAL RESULTS

In Figs. 1-4 are given the results of modulus determinations on this cold-rolled strip and drawn rod, each plotted result representing the average of at least twelve modulus values, i.e. six on duplicate specimens.

(a) Copper

From Fig. 1 it will be seen that the value of the Young's modulus of H.C. copper strip varies with the three directions of testing in relation to the rolling direction. At 90° to the rolling direction it increases progressively with the degree of deformation, while at 45° it progressively decreases. In the rolling direction, however, there is a definite fall, reflected in a decrease in the values from 17.3×10^6 lb./in.² for the metal in the annealed state to 16.3×10^6 lb./in.² as a result of a 5% cold-rolling reduction, and thereafter there is a progressive increase with further

are greater than the longitudinal ones suggests a pre-dominance of the primary texture.

Using the known values of the elastic constants of the copper lattice, and assuming the stress to be homogeneous, it is possible from the relative values of modulus for the three directions of testing to estimate the approximate proportions of primary and secondary rolling textures and of residual random texture.⁴ After a rolling reduction of 90% the estimated proportions are 0.4, 0.25, and 0.35, respectively, which lead to a computed value of 15.3×10^6 lb./in.² for the randomly orientated component in the cold-worked condition, as compared with 17.5×10^6 lb./in.² in the initial annealed 0.3 in. stock. That is, the effect of lattice distortion and work-hardening, as such, without the complication of preferred orientation effects, is to reduce the elastic modulus.

An initial fall in modulus values of the type observed for copper strip in the rolling direction, as shown in

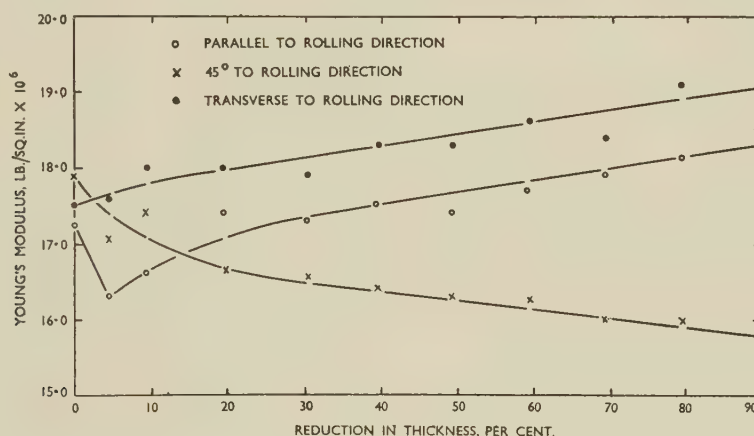


FIG. 1.—Influence of Cold Rolling on the Young's Modulus of H.C. Copper.

rolling. After a rolling reduction equivalent to 90% in thickness, the difference between maximum and minimum modulus values in different directions is considerable, amounting to no less than 3.4×10^6 lb./in.².

These results are in contrast with the effect of cold rolling on tensile strength,¹ which, as a consequence of work-hardening, increases progressively and continuously in all directions, the effect of anisotropy being reflected in divergent strength values in different directions after heavy rolling reductions.

Apart from the initial fall in modulus shown by specimens cut in the rolling direction, an effect discussed more fully later, it appears that the difference between the modulus values in the three directions after cold rolling is consistent with the progressive development of the primary and secondary rolling textures, $\{110\} \langle 112 \rangle$ and $\{112\} \langle 111 \rangle$, typical of rolled copper,² and with the known anisotropy of the copper lattice.³ The progressively decreasing values in the 45° direction could result from the development of either texture, but the fact that transverse values

Fig. 1, has also been noted after small extensions by Smith,⁵ who attributed it to the generation of mobile lattice dislocations. Evidence described later lends support to Smith's view concerning the cause of this initial fall; furthermore, by metallographic examination⁶ of copper rolled with progressively increasing reductions it has been demonstrated that deformation during reductions up to about 25% occurs principally by a complex slip mechanism involving generation and movement of dislocations. With reductions of the order of 50% and more, however, the metallographic evidence is that deformation then occurs by shear upon planes situated transversely to the rolling direction and inclined at about 30° - 35° to the strip surface. Such shear results in the development of structural discontinuities. By examination of longitudinal sections, traces of the shear planes can be seen in one direction only in any one crystal, and it has been suggested⁷ that this indicates shear on $\{100\}$ planes of crystals of the secondary $\{112\} \langle 111 \rangle$ texture. The fact that the modulus in heavily rolled copper strip is greater in the transverse direction than

in the rolling direction can thus be interpreted as an indication that the shear planes are actually planes of weakness and that the proportion of the secondary $\{112\}$ $\langle 111 \rangle$ texture is probably a little more than 0.25, as estimated, without consideration of the possible effect of structural discontinuities. As will be indicated later, the discontinuities are of greater significance in heavily rolled brass.

The effect of cold drawing on the modulus of annealed copper rod is, as illustrated in Fig. 2, similar to that of cold rolling on the modulus values measured in the rolling direction; that is, after an initial

to that of rolling (Fig. 3) is very similar to that observed for copper (Fig. 1), in as much as there is a progressive decrease and increase, respectively, but in the rolling direction the results for the two metals differ somewhat. The decrease in modulus at 0° to the rolling direction observed with copper after a small reduction is not evident with brass strip, which shows a progressive increase in modulus up to a maximum corresponding to a rolling reduction of about 20% and thereafter a steady decrease, so that after reductions exceeding about 60% the values approximate to those observed in test-pieces cut at 45° to the rolling

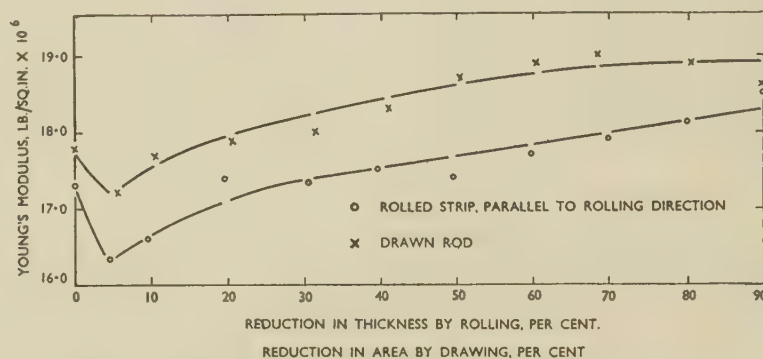


FIG. 2.—Influence of Cold Rolling and Cold Drawing on the Young's Modulus of H.C. Copper.

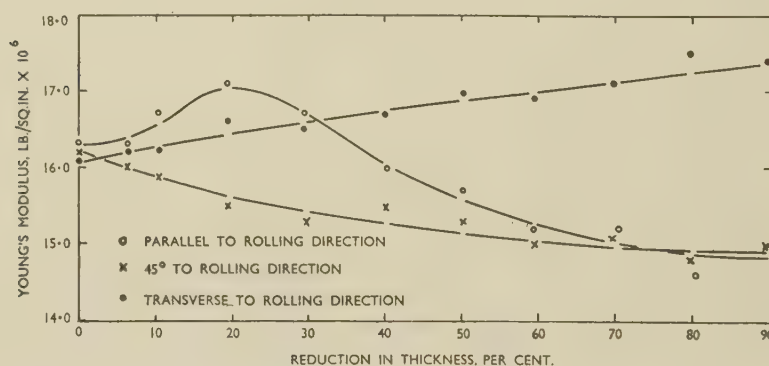


FIG. 3.—Influence of Cold Rolling on the Young's Modulus of 70 : 30 Brass Strip.

decrease the modulus progressively rises, although values for the rod are somewhat higher than those for strip at all corresponding stages. The higher values for rod are explained by the predominance of crystals having a $\langle 111 \rangle$ zone axis, the direction of maximum modulus, parallel to the rod axis, and it is significant in this respect that, for deformation in excess of about 20% in thickness or area, the actual modulus at corresponding reductions for drawn rod approximates closely to the value measured at 90° to the rolling direction in cold-rolled strip, for the primary rolling texture has a $\langle 111 \rangle$ axis in the transverse direction.

(b) Brass

The effect of cold rolling on Young's modulus of 70 : 30 brass as measured in directions at 45° and 90°

direction. However, in experiments described in Section IV, involving modulus determinations on brass after close intervals of extension, an initial fall in modulus was, in fact, found.

As with copper, the effect of cold rolling on the elastic modulus of brass is quite different from that on such other properties as limit of proportionality, proof stress, and tensile strength,⁸ all of which, as a consequence of work-hardening, increase progressively in all directions, anisotropic effects manifesting themselves in divergent values in different directions after heavy rolling reductions.

The progressively greater differences between modulus in the 45° and 90° directions with increasing reductions can be accounted for by the development of the primary $\{110\}$ $\langle 112 \rangle$ rolling texture typical

of rolled brass.² The relatively high modulus values at 0° after a reduction of 20% is explained by the development of an intermediate rolling texture with the $\langle 111 \rangle$ axis of maximum modulus in the rolling direction, as revealed by X-ray glancing photographs of transverse sections. The very marked decrease in the 0° modulus values with reductions in excess of this amount would suggest the presence of planes of easy shear situated transverse to the rolling direction and inclined at about 30°–35° to the strip surface, and that these have a more pronounced influence on the modulus of brass than on the modulus of copper. The most probable explanation of this effect is that the operative shear planes are of different crystallographic character in the two materials. Whereas in

on Young's modulus, without the additional and complicating effect of preferred crystalline orientation. The results, plotted in Fig. 4, indicate a small but significant fall in modulus after a rolling reduction of 5% from 9.75×10^6 lb./in.² for the initial annealed material to 9.4×10^6 lb./in.². The modulus then remains constant in value with increasing reduction to 40%, but thereafter decreases to 8.9×10^6 lb./in.² with a 90% reduction. As with copper, the first initial drop in value can be attributed to mobile lattice dislocations and the lower values for more heavily rolled aluminium strip to the presence of planes of easy shear, as in copper and brass. This latter view was confirmed by testing aluminium strip cold rolled 90% in three directions, namely, at 0°, 45°, and 90° to the rolling direction, when it was observed that specimens cut in the last direction gave distinctly higher modulus values.

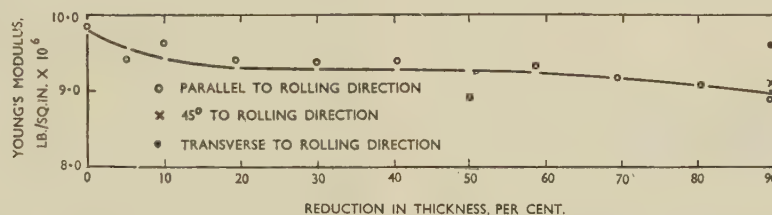


FIG. 4.—Influence of Cold Rolling on the Young's Modulus of Super-Pure Aluminium Strip.

longitudinal microsections of copper, traces of intense shear appear exclusively in one direction and also only in about half the crystals, two symmetrical traces appear in practically every crystal of rolled brass.⁹ Furthermore, the traces in copper may be considered as evidence of shear on $\{100\}$ planes in a $\langle 110 \rangle$ direction of the secondary $\{112\}$ $\langle 111 \rangle$ rolling texture. Such shear is analogous to the secondary slip system observed in the deformation of aluminium.¹⁰ The shear system in heavily rolled brass, on the other hand, is $\{112\}$ $\langle 110 \rangle$, and since $\{112\}$ slip has never been observed in face-centred cubic metals, it is possible that the $\{112\}$ shear planes are also planes of incipient fracture. This would, in fact, explain the low modulus values of brass in the rolling direction. The incipient-fracture planes would have no influence on modulus values measured in the transverse direction, but would exercise progressively greater effect as the direction of the test-piece approached that of rolling.

Because of the pronounced effect of the structural imperfections in heavily rolled brass, it is not possible to compute, as was done for copper, the proportions of the material with rolling texture and with random orientation and the modulus value of the latter.

(c) Aluminium

The aluminium lattice is only slightly anisotropic elastically, the ratio of maximum modulus in the $\langle 111 \rangle$ direction to the minimum value in a $\langle 100 \rangle$ direction being 1.2. In consequence, tests on specimens of cold-rolled aluminium reveal in a direct manner the influence of lattice distortion and structural defects

and 90° to the rolling direction, when it was observed that specimens cut in the last direction gave distinctly higher modulus values.

IV.—EFFECT OF DEFORMATION BY EXTENSION AND COMPRESSION

To examine the effect of small strains in more detail, several further experiments were carried out. These included modulus measurements on tensile test-pieces of copper and brass after simple plastic extensions within the range 0–20% elongation, on copper test-pieces machined from a rod compressed about 2% and on copper test-pieces cut in different directions from strip extended 2%.

The first of these experiments was designed to determine the precise relationship between strain and modulus and to establish whether or not the initial fall in modulus was possibly associated with the development of preferred orientation of crystals. For this purpose the $1\frac{1}{2}$ in. hot-rolled slab of H.C. copper used for the study of the effect of rolling was first cold rolled to a thickness of $\frac{3}{4}$ in. Standard tensile test-pieces conforming to B.S. 18 were machined from the $\frac{3}{4}$ in. slab in the cold-rolled condition and annealed for 1 hr. at 500° C., so that modulus measurements could be made on completely strain-free specimens. X-ray and metallographic examination indicated that the material in this condition was recrystallized to an almost random structure. Elastic modulus values were determined on a specimen in the annealed state and after several plastic extensions in a tensile-testing machine to a maximum elongation of 20%. The

observed values, each again being the average of six, are shown in Fig. 5. The sharp fall in modulus with small plastic extension observed with copper on cold rolling and drawing is thus confirmed, a minimum value occurring after about 3% extension. Thereafter the modulus increased progressively with extension.

X-ray and metallographic examination of sections normal to the direction of elongation, before and after

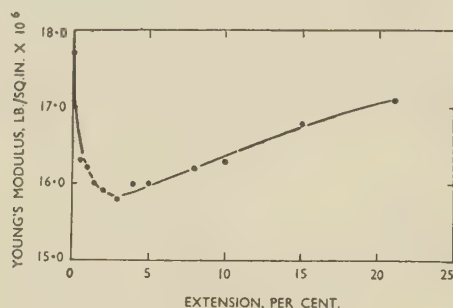


Fig. 5.—Influence of Plastic Extension on the Young's Modulus of H.C. Copper.

various extensions, revealed no significant change in structure that would account for the initial fall in modulus, but after an extension of 20% $\langle 111 \rangle$ and $\langle 100 \rangle$ fibre textures were developed to an appreciable extent, the former predominating. Since the $\langle 111 \rangle$ direction is that of maximum tensile modulus, the increase in modulus with elongation in excess of 3% can be attributed to crystal anisotropy and development of textures.

From the similarity in crystal structure of copper and brass, and in their degree of elastic anisotropy, it would be expected that the effect of cold deformation on the modulus of the two materials would be essentially the same. The effect of simple extension on the modulus of brass was studied in detail to determine whether this was so, although in examining the influence of rolling after reductions at comparatively wide intervals no significant initial fall of modulus in the rolling direction had been observed (Fig. 3). For this purpose tensile specimens were machined from 0.3 in. brass strip used in the rolling experiments and annealed at 550°C. for 1 hr. Modulus values after different extensions are plotted in Fig. 6, and it can be seen that, as with copper, there is a sharp initial fall in modulus. The minimum value for brass, however, occurs at an extension of about 1% as compared with about 3% for copper. Thereafter the modulus increases with extension to 17.5×10^6 lb./in.² after 20% extension.

X-ray examinations were made of specimens in the annealed state and after extensions of 1 and 20%. The annealed material showed a random orientation of crystals. No significant change in orientation was observed after 1% extension, but after 20% extension a definite fibre texture had developed, the crystals being orientated with either a $\langle 111 \rangle$ or a $\langle 100 \rangle$ axis parallel to the tension axis, the $\langle 111 \rangle$

texture of maximum modulus predominating. The primary rolling texture in brass has a $\langle 111 \rangle$ axis in the transverse direction, while the easy-shear or incipient-fracture planes, being parallel to the transverse axis, exercise no effect on modulus values measured in the transverse direction, and it will be noted that the transverse modulus value of brass strip cold-rolled 90% corresponds exactly to that observed with brass after 20% extension.

In the present experiments the initial fall in modulus in the direction of principal strain, observed with both copper and brass after small plastic extensions, is not associated with any observable change in crystal orientation. Since, however, plastic deformation also gives rise to residual stresses, it is possible that such stresses might be the cause of the observed initial fall. If this were so, it would be reasonable to expect that tensile and compressive strains would have opposite effects. The influence of small compressive strains on the modulus of H.C. copper rod was therefore examined.

Four adjacent $3\frac{1}{2}$ in. lengths of the $\frac{7}{8}$ in. dia. copper rod prepared for study of the effect of cold drawing, were annealed for 1 hr. at 500°C. Two of these were machined to small round test-pieces of $1\frac{1}{2}$ in. gauge-length, while the other pair were axially compressed about 2% and then carefully machined for tensile testing. Modulus measurements revealed that a small plastic strain by compression is also accompanied by a definite decrease in modulus, from an initial value of 17.5×10^6 lb./in.² to 16.1×10^6

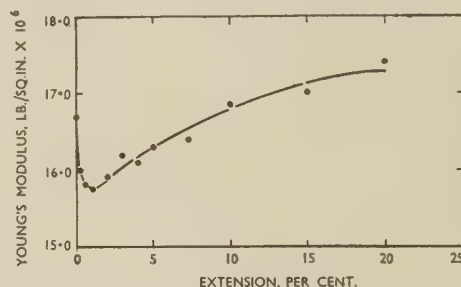


Fig. 6.—Influence of Plastic Extension on the Young's Modulus of 70 : 30 Brass.

lb./in.², which is of the same order of magnitude as that produced by the same strain in tension. The main conclusion that can be drawn from this observation is that the decrease in modulus is independent of the nature of the plastic strain and consequent residual stress, that is, whether these are tensional or compressional.

Although the fall in modulus is observed after small plastic strains, produced by cold drawing, simple tension, or by compression, it does not occur in rolling in test-pieces cut transverse to the rolling direction. The effect is therefore directional, the directionality being related in some way to the principal axis of strain. To examine this further, a piece of 8×0.2 in. hot-rolled H.C. copper strip was cold rolled to a thickness of 0.1 in. and annealed for 1 hr. at 500°C. Part

was retained in the annealed condition and the remainder extended 2% in a stretching machine. From both the annealed and stretched samples duplicate tensile test-pieces were cut at 0°, 55°, and 90° to the axis of extension, which was coincident with the rolling direction. The test-pieces were taken in these particular directions, since a small plastic extension e is, on the basis of no change in volume, associated with a contraction of $\frac{1}{2}e$ perpendicular to the axis of extension and with zero extension at 55°. The modulus values at 0°, 55°, and 90° to the stretching direction were 18.8, 16.8, and 17.8×10^6 lb./in.², respectively, for specimens in the annealed condition, and 16.7, 17.0, and 17.7×10^6 lb./in.² after 2% extension.

The modulus values for the annealed test-pieces in the various directions indicate some measure of anisotropy in the initial strip. However, after stretching, a definite decrease in modulus is observed in the direction of stretching but no significant change in the other two directions. These observations would appear to confirm the view that the fall in modulus associated with small plastic strains is due to mobile dislocations generated by the strain. Thus, dislocations produced by extension in a particular direction would be expected to have maximum mobility under applied stress, either tensional or compressional, in the same direction, while, on the other hand, the effect of such dislocations on modulus measured in directions well removed from the extension axis would be insignificant, as the results of these experiments have shown.

V.—CONCLUSIONS

The results of this work indicate that the main effects of cold deformation on the Young's modulus of copper, brass, and aluminium may be summarized as follows:

(1) A small plastic strain induces, in the direction of strain, a decrease in modulus of all three materials, and the fact that the decrease is observed in copper,

for example, after small strains in both compression and extension and only in directions of testing close to the principal axis of strain, provides confirmation of the view that the decrease is due to the generation of mobile dislocations.

(2) With rolling reductions of about 50% or more, deformation occurs by a shear mechanism other than normal crystallographic slip, generating structural discontinuities larger in scale than dislocations in the form of planes of easy shear situated transverse to the direction of rolling and inclined at 30°–35° to the strip surface. The presence of such planes is associated with a further decrease in average modulus values, and in lower values for specimens tested in the rolling direction as compared with those tested transverse to this direction. The latter effect is particularly striking for brass, and it is suggested that the planes of easy shear in this material might represent incipient fractures.

(3) Rolling results in the progressive development of preferred orientation of the crystal structure, and for copper and brass, which are elastically anisotropic, in appreciable differences in Young's modulus in different directions of testing, but this effect is not nearly so pronounced with aluminium, which is almost isotropic.

REFERENCES

1. M. Cook and T. Ll. Richards, *J. Inst. Metals*, 1941, **67**, 203.
2. Hsun Hu, P. R. Sperry, and P. A. Beck, *Trans. Amer. Inst. Min. Met. Eng.*, 1952, **194**, 76.
3. E. Goens, *Ann. Physik*, 1940, [v], **38**, 456.
4. C. S. Barrett, "Structure of Metals", 2nd edn., p. 533. 1952: New York and London (McGraw-Hill).
5. A. D. N. Smith, *Phil. Mag.*, 1953, [vii], **44**, 453.
6. M. Cook and T. Ll. Richards, *J. Inst. Metals*, 1940, **66**, 1.
7. M. Cook and T. Ll. Richards, *ibid.*, 1950–51, **78**, 463.
8. M. Cook, *ibid.*, 1937, **60**, 159.
9. M. Cook and T. Ll. Richards, *ibid.*, 1943, **69**, 351.
10. W. Boas and E. Schmid, *Z. Physik*, 1931, **71**, 703.

By J. R. BROWN,† B.A.

SYNOPSIS

The course of the solid-solubility curve of cadmium in zinc has been followed by measurement of the lattice parameters of quenched alloys. The solid solubility at the eutectic temperature is found to be 1.07 at.-% (1.83 wt.-%), compared with 1.23 at.-% (2.10 wt.-%) reported by earlier workers. The partial molal energy and entropy of solution have been calculated from the experimental results and found to be 6915 cal. and 3.88 cal. deg.⁻¹, respectively.

I.—INTRODUCTION

In a dilute solid solution each solute atom is the centre of a region of strain extending for a radius of several interatomic distances. The misfit gives rise to an increase in the potential energy of the lattice. A change of entropy also occurs, not only because of the randomness of location of the solute atoms, but also because the vibration frequencies of the atoms in the strained region are changed.

Lumsden¹ has made an estimate of the ratio of energy to entropy increases due to lattice distortions in close-packed crystals. By making a number of simplifying assumptions, he finds:

$$\frac{\Sigma(\Delta E)}{\Sigma(\Delta S)} = \frac{3R\kappa}{4\alpha^2 V} \cdot \cdot \cdot \cdot (1)$$

where $\Sigma(\Delta E)$ is the energy increase, $\Sigma(\Delta S)$ the entropy increase, R the gas constant, κ the compressibility, α the thermal-expansion coefficient, and V the volume/g.-atom.

The theory may be checked experimentally, since an estimate of $\Sigma(\Delta E)$ and $\Sigma(\Delta S)$ can be deduced from the thermodynamic properties of dilute solutions. The heat of solution in the liquid state is a measure of the intrinsic potential energy between like and unlike atoms. In the solid state, the heat of solution includes the energy due to the misfit. Likewise, the entropy of solid solution is greater than that of liquid solution (the ideal value) by the entropy due to the misfit.

Few suitable binary metallic systems have been investigated thoroughly enough for estimates to be made of the energies and entropies of solid and liquid solutions. The zinc-cadmium system, however, has been very completely studied, and Lumsden has analysed the experimental evidence and obtained energies and entropies of solution to verify his theory.

The heat and entropy of solid solution may be obtained from a knowledge of the course of the solid-solubility curves, if Henry's and Raoult's laws are assumed to hold. When the solutions are dilute, as

in the solid solutions of zinc and cadmium, these assumptions are reasonable.

The published work of Jenkins,² Stockdale,³ and Boas⁴ on the solid solution of cadmium in zinc is not consistent with these assumptions. For this reason the present redetermination of the solid-solubility curve was undertaken, and more accurate values of the partial molal energy and entropy of solution of cadmium in zinc were obtained. The experimental method used was that of lattice-parameter measurements on quenched alloys.

II.—EXPERIMENTAL PROCEDURE

1. PREPARATION OF THE ALLOYS

High-purity zinc (99.999%) and high-purity cadmium (99.99%) were melted together in a graphite crucible and cast at as low a temperature as possible to minimize loss of cadmium by evaporation. An iron mould was used to form ingots 10 cm. long and 1 cm. in dia. These were examined spectrographically to check whether contamination had occurred during preparation.

The ingots were then sealed under vacuum in glass tubes and annealed for 10 days at 250° C. After annealing, half of each ingot was used for chemical analysis, the other half being retained for X-ray examination. Chemical analysis was carried out on 10-g. samples, and close agreement with the nominal compositions was found. The alloys covered the range 0–3% cadmium by weight in steps of 0.4%.

2. X-RAY TECHNIQUE

A 19-cm.-dia. powder camera was used with specimens in the form of fine filings. The zinc-rich phase under examination having a hexagonal lattice, graphical methods of refining lattice constants could not easily be applied; instead an analytical extrapolation due to Cohen (see, for example, Buerger⁵) was

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applied. A term $D \sin^2 2\theta$ was added to the Bragg equation, giving:

$$\sin^2 \theta = \frac{4s}{3} \cdot A + l^2 C + D \sin^2 2\theta \quad (2)$$

where $A = \frac{\lambda^2}{4a^2}$, $C = \frac{\lambda^2}{4c^2}$, $s = h^2 + hk + k^2$. A and C can be found and D eliminated by measuring the Bragg angles of three reflections. This method removes the eccentricity error, but the absorption error is not completely corrected. Further correction terms can be added and the least-squares refinement made, but the extra computational work involved is considerable. Measurements on pure zinc showed that equation (2) gave results which were accurate enough for the present purpose. Cobalt radiation was chosen for the work, the $K\alpha$ reflections from the (20.3), (10.5), and (11.4) planes being measured at Bragg angles of 71° , 80° , and 81° , approximately. The value 1.78529 kX units was taken for the wave-length of $\text{CoK}\alpha_1$ radiation, and all the results were corrected to a temperature of 25°C ., using the values of the expansion coefficients found by Lumsden (unpublished):

$$\begin{aligned}\alpha_a &= 1.2 \times 10^{-5}/^\circ\text{C} \\ \alpha_c &= 5.7 \times 10^{-5}/^\circ\text{C}.\end{aligned}$$

The results of five measurements on pure zinc are given in Table I.

TABLE I.—*Lattice Constants of Pure Zinc at 25°C .*

a , kX	c , kX	a , kX	c , kX
2.65926	4.93691	2.65900	4.93702
2.65922	4.93665	2.65934	4.93650
2.65946	4.93677		

For each alloy in the present series, four separate determinations of lattice constants were made, and from these the standard error of the mean was calculated:

$$\begin{aligned}S_a &= 0.0001 \\ S_c &= 0.0001\end{aligned}$$

So for pure zinc at 25°C .:

$$\begin{aligned}a &= 2.6592(6) \pm 0.0001 \\ c &= 4.9367(7) \pm 0.0001\end{aligned}$$

If these figures are corrected for refraction of X-rays, the values:

$$\begin{aligned}a &= 2.6593(4) \text{ kX} \\ c &= 4.9369(1) \text{ kX}\end{aligned}$$

are obtained, agreeing well with the usually accepted results of Jette and Foote⁶:

$$\begin{aligned}a &= 2.65941 \text{ kX} \\ c &= 4.93685 \text{ kX}\end{aligned}$$

It is clear, then, that any systematic error due to incomplete correction for absorption is small.

3. HEAT-TREATMENT OF THE ALLOYS

After the lump-anneal, filings were taken from the ingots and sealed in small evacuated glass tubes which were annealed for not less than 24 hr. at the required temperature and then quenched into water. Initially a number of tests were carried out to check the efficiency of the heat-treatment. Filings from the same alloy were annealed for different periods before quenching, one batch for 24 hr., another for 48 hr. One batch of filings was photographed immediately after quenching and again 24 hr. later. Finally, filings from three different parts of one ingot were annealed and quenched. No significant differences in lattice constants were found in any of these tests.

It was assumed that the filings underwent no change of composition during annealing, and the analyses of the original ingots were taken as holding for the filings. For strict accuracy, the filings used for the X-ray measurements should also be used for the analysis. In the present case, since the cadmium content of the alloys was low, the desired accuracy was obtained only by analysis of 10-g. samples. The only possible source of systematic error involved in this procedure is through loss of cadmium by vaporization. An estimate of the possible magnitude of this error during annealing at 270°C . shows that in a 1% cadmium alloy it would, at the most, amount to only $10^{-9}\%$. Errors due to contamination would not be systematic and, if significant, would have been detected by the repeated measurements.

Measurements were first made on alloys of known cadmium content quenched from temperatures near to that of the eutectic, so that the relationship between lattice constants and percentage cadmium dissolved could be determined. The solid-solubility curve was then found by measuring lattice constants of a saturated alloy quenched from a known temperature. The temperature of the annealing furnace could be kept constant to within $\pm 1^\circ \text{C}$. for long periods, and was measured by a specially calibrated Chromel/Alumel thermocouple and potentiometer to within 1°C .

III.—EXPERIMENTAL RESULTS

Fig. 1 shows the measured values of the a and c lattice constants of alloys quenched from a temperature near to that of the eutectic, each point representing the mean of four determinations. These graphs were used to find the dissolved cadmium content of saturated alloys quenched from known temperatures. Table II shows the a and c parameter measurements obtained, together with the estimated percentage of cadmium in solution. Two separate measurements were made on each batch of filings quenched. The determinations from the c parameter were given double the weight of those from a , since the c axis was measured with greater accuracy. The estimated accuracy of the solid-solubility figures is 0.02 at.-%.

In an ideal solid solution, the heat of mixing is zero and the entropy of solution is the ideal value due simply to the increased randomness of location of the atoms. In a real solution, such as that of cadmium in zinc, the partial molal free energy of cadmium exceeds that for the solute in an ideal solution by an amount known as the thermodynamic deviation, y .⁷

$$y = RT \ln \gamma_{\text{Cd}}$$

where γ_{Cd} is the activity coefficient of cadmium in the solution. Henry's law is assumed to hold for the solute and Raoult's law for the solvent, so that the

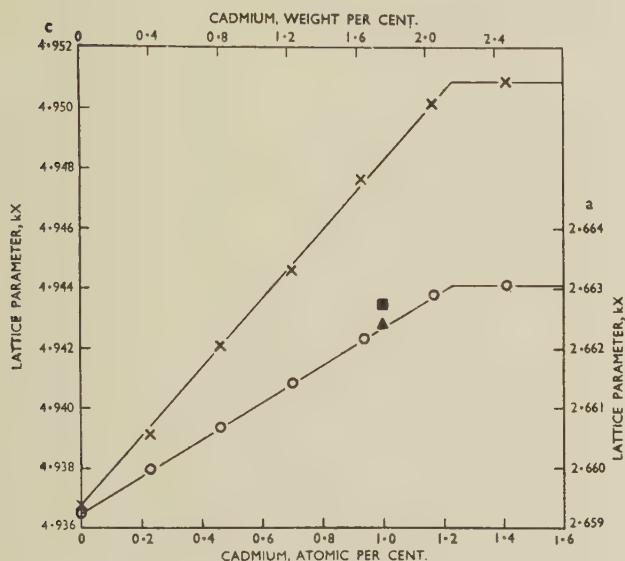


FIG. 1.—Lattice Parameters of Zinc-Cadmium Alloys.

KEY.
 ○ a parameter, × c parameter.
 ▲ " from Vegard's law, ■ " from Vegard's law

activity coefficient of cadmium in solid zinc saturated with cadmium is:

$$\gamma_{\text{Cd}} = N'_{\text{Cd}}/N_{\text{Cd}}$$

where N_{Cd} and N'_{Cd} are the atomic fractions of cadmium in the zinc-rich and cadmium-rich phases, respectively.

$$y = RT \ln \gamma_{\text{Cd}} = \Delta H - T(\Delta S + R \ln N_{\text{Cd}}) \quad (3)$$

where ΔH is the partial molal heat of solution of the cadmium and $(\Delta S + R \ln N_{\text{Cd}})$ is the partial molal deviation from ideal of the entropy of solution.

It is assumed that the latter is constant over the range of compositions of stable solid solutions, so that equation (3) represents a straight line with slope equal to the entropy of solution, and intercept on the y axis equal to the heat of solution. The activity coefficient was calculated, using the values of N'_{Cd} found by Stockdale.³ It should be noted that errors in the value of N'_{Cd} do not greatly affect the value of γ_{Cd} .

TABLE II.—Lattice Constants of Saturated Alloys.

Temp., °C.	a , kX	c , kX	Cadmium, at.-%		
			From a	From c	Weighted Mean
94	2.65944 2.65926	4.93747 4.93718	0.06 0.00	0.07 0.04	0.05
152	2.65998 2.65987	4.93910 4.93877	0.24 0.20	0.21 0.18	0.20
172	2.66013 2.66017	4.94031 4.93943	0.29 0.30	0.31 0.23	0.28
190	2.66062 2.66037	4.94104 4.94114	0.43 0.36	0.37 0.38	0.38
210	2.66050 2.66104	4.94225 4.94227	0.41 0.59	0.48 0.48	0.49
235	2.66154 2.66137	4.94479 4.94448	0.74 0.69	0.69 0.67	0.69
253	2.66217 2.66213	4.94716 4.94716	0.96 0.95	0.90 0.90	0.92
259	2.66239 2.66226	4.94797 4.94763	1.03 0.99	0.97 0.94	0.97
271	2.66282 2.66238	4.94912 4.94905	1.17 1.03	1.08 1.07	1.08

Fig. 2 shows $RT \ln \gamma_{\text{Cd}}$ plotted against T , and the line drawn fits the equation:

$$RT \ln \gamma_{\text{Cd}} = 6915 - 3.88T$$

from which

$$\Delta H = 6915 \text{ cal.}$$

$$\Delta S + R \ln N_{\text{Cd}} = 3.88 \text{ cal. deg}^{-1}.$$

The solid-solubility curve calculated from this equation is shown in Fig. 3, together with the experimen-

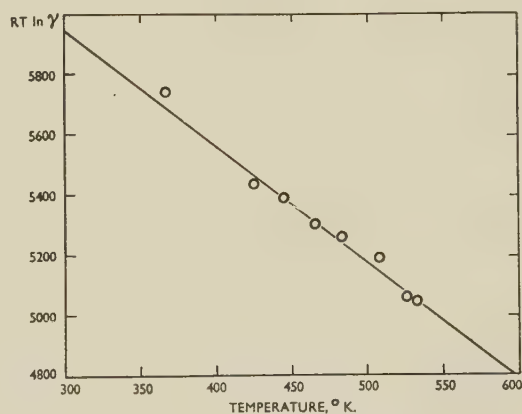


FIG. 2.—Variation of $RT \ln \gamma_{\text{Cd}}$ with Temperature.

tally determined points and those of earlier workers. The solubility at the eutectic temperature found in the present work is 1.07 at.-%, compared with 1.23 at.-% found by Boas,⁴ using X-rays, and similar figures found by Jenkins² and Stockdale³ by microscopic methods. The difference is well outside the estimated

experimental error of the present work. In view of the difficulty of fitting the results of the previous workers to an equation of the form (3), and the good fit of the present results, it is considered that the earlier work must have been inaccurate.

An attempt was made to measure the solid solubility of zinc in cadmium-rich alloys, using X-rays in

this is a case where it might reasonably be expected to hold, for zinc and cadmium are closely similar in crystal structure and electronic constitution.

The energy and entropy values found are shown in Table III, together with those obtained by Lumsden.

TABLE III.—Partial Energies and Entropies of Solution of Cadmium in Zinc.

Origin	Partial Molal Energy, ΔH , cal.	Partial Molal Entropy, cal./degree
Present work	6915	3.88
Lumsden, solid alloys . . .	6560	3.40
Lumsden, liquid alloys . .	2080	0.00
Difference due to lattice distortions: Present work .	4835	3.88
Lumsden	4480	3.40

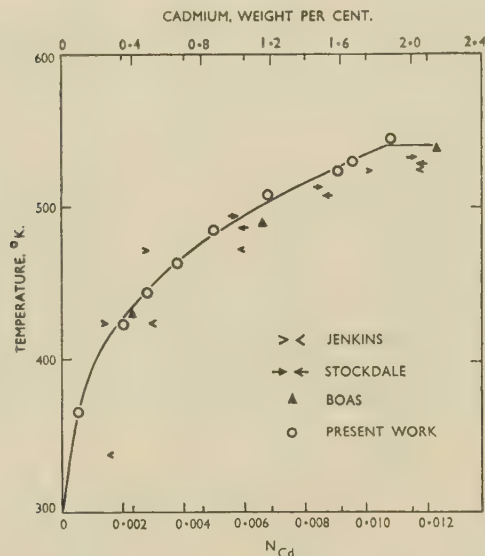


Fig. 3.—Solid-Solubility Curve of Cadmium in Zinc.

the same way, but it was not possible, by quenching, to retain the zinc in solution long enough for diffraction photographs to be taken.

IV.—DISCUSSION

Fig. 1 shows that Vegard's law is not obeyed in this solid solution. In the case of the a axis, the expansion of the lattice is precisely that expected from the simple additivity law, but that of the c axis is greater. Using the additivity law, the lattice constants of a 1 at.-% solution of cadmium in zinc are found to be 2.6624 and 4.9435, compared with the experimental figures of 2.6623 and 4.9482 kX. Although Vegard's law has proved to be the exception rather than the rule,

In the liquid state, the heat of mixing is determined by the interatomic potential energies between like and unlike atoms. In the solid solution the heat of mixing is increased by the contribution due to the disturbances of the regularity of the atomic packing. Similarly, as a result of the looseness of packing and the consequent lowering of the vibration frequencies of the atoms, the partial entropy of solution of the cadmium is greater in the solid state than in the liquid.

The ratio of energy to entropy increase due to lattice distortions is 1250° K., compared with the value derived for zinc from equation (1) of 1500° K. Lumsden's earlier estimates of the energy and entropy increases, while they differ appreciably from ours, have a similar ratio, namely 1310° K. The present investigation has not improved the agreement with the theory; this must be attributed to the fact that the theory is strictly applicable only to isotropic metals, which zinc certainly is not.

The agreement between the experimental and calculated solubility curves is now very good, and lends confidence to both the experimental results and the theory.

ACKNOWLEDGEMENTS

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REFERENCES

1. J. Lumsden, "Thermodynamics of Alloys", Chapter 19. 1952: London (Institute of Metals).
2. C. H. M. Jenkins, *J. Inst. Metals*, 1926, **36**, 63.
3. D. Stockdale, *ibid.*, 1930, **44**, 75.
4. W. Boas, *Metallwirtschaft*, 1932, **11**, 603.
5. M. J. Buerger, "X-Ray Crystallography", Chapter 20. 1942: New York (John Wiley and Sons, Inc.).
6. E. R. Jette and F. Foote, *J. Chem. Physics*, 1935, **3**, 605.
7. J. Lumsden, *loc. cit.*, Chapters 10 and 13.

GROWTH TWINS IN CRYSTALS OF LOW CO-ORDINATION NUMBER *

1565

By E. BILLIG,† D.Sc.Tech., M.I.E.E.

SYNOPSIS

Steady growth of a monocrystalline ingot of germanium proceeds from the melt essentially as a perfect continuation of the crystal lattice already formed. However, growth twins are frequently observed which seem to be caused by some unevenness in the growth rate, and the following is suggested as one possible mechanism for their formation. Assuming that growth has momentarily been stopped, then the crystal will, on resumption of growth, tend to form a twin if the orientation of the preferred growth planes, i.e. the close-packed (111) lattice planes, is nearer to the main temperature gradient in the twinned than in the original crystal. Owing to the perfect atomic fit at the twin plane, the additional energy required is very small and does not impede the formation of the twin, especially if the start can be made as a co-operative phenomenon simultaneously over a long line rather than from a single point. The small amount of energy required to initiate twinning could be supplied by fluctuations in the temperature and the thermal stresses caused by them.

Structural defects often start from the intersection of two twin planes, owing to the lattice misfit at that line. This is particularly noticeable in silicon ingots grown along the [211] direction, which are likely to contain twin bands persisting along the growth direction.

I.—POSSIBLE TWINNING MECHANISMS

ONE of the more troublesome features in the growth of monocrystalline silicon is the frequent occurrence of twins. Relatively little is known about the cause of growth twins, and their occurrence is frequently regarded as a somewhat haphazard event. Fig. 2 (Plate IX), however, indicates that under comparable conditions twinning will recur quite definitely. In this case, an ingot of silicon was divided evenly by a twin band *A* passing through the vertical axis which was in the [211] direction. Further twinning then occurred from point *b* in the left half of the ingot about a twin plane making an angle of 70° 32' with the vertical; a little later, precisely the same type of twinning recurred at point *B* in the right half, which was, of course, the exact image of the left.

There are, in principle, two possibilities of twins occurring during growth:

(1) The solid might actually grow as a perfect monocrystal and twinning, due to some mechanical stress, might occur at a later stage, i.e. in the solid state. In this case, the change would presumably occur very soon after solidification when, at temperatures close to the melting point, the resistance of the crystal to deformation, i.e. its critical shear stress, is very low.

Large stresses can arise in a crystal growing from its melt, owing to the change in volume which occurs on solidification. The materials under discussion have a very open crystal structure and on solidification expand by appreciable amounts, about 5–10% in volume. So if the melt is confined by the walls of a crucible, or by a frozen skin on the surface, very large

pressures can be set up, sufficient to crack the crucible. Such ingots usually display large numbers of twins and other defects in their structure.

If the crystal grows freely from the melt, as for instance in the crystal-pulling technique, these stresses are largely eliminated, and the main forces then remaining are attributable to surface and interfacial tension. Fig. 1 illustrates the three tensions,

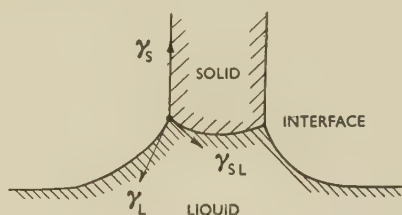


FIG. 1.—Surface and Interface Tensions Acting on Solid/Liquid Interface.

γ_s , γ_L , γ_{SL} , acting on the growing face of the crystal, i.e. at the interface between solid and melt. The precise values of these tensions are not known, but their order of magnitude is between 100 and 1000 dynes/cm. If these forces were taken up by a surface film a few atomic layers thick, they would be sufficient—of the order of 10 kg./mm.²—to overcome the mechanical strength of the ingot at these high temperatures.

In the crystals grown in the course of the present work, no direct evidence was obtained which would support this mechanism of twinning, i.e. after solidification of the ingot.

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(2) An alternative possibility is that twinning might occur directly as the crystal grows from the melt, i.e. during the deposition of individual atomic layers. In the crystal structure under discussion—diamond or zinc blende—twinning is always observed about one of the {111} family of lattice planes acting as a twin plane.* In a diamond crystal there are four types of such ("octahedral") planes belonging to the same family, inclined at $70^{\circ} 32'$ to each other. The bonding in these materials is strongly covalent, and interaction between atoms can, to a first approximation, be assumed to be confined to nearest neighbours. Twinning about a (111) plane is a simple stacking fault; it gives perfect fit of the lattices on either side, i.e. it leaves all distances between nearest neighbours, and all bond angles undisturbed. Very little energy is therefore required—only that due to interaction between second-nearest neighbours—to initiate such twinning: a monocrystal growing with a certain crystallographic orientation can readily swing over to one of four other orientations by this mechanism.

II.—OBSERVED BEHAVIOUR OF GERMANIUM AND SILICON

1. CORRELATION OF {111} PLANES WITH TEMPERATURE GRADIENT

In the following argument, one possible mechanism is suggested which might account for the occurrence of at least some of the growth twins. It has recently been established at this laboratory that growth in the crystals of the cubic structures mentioned proceeds preferentially as an extension of the {111} lattice planes, these being the ones of highest atomic packing. It is therefore suggested that in any monocrystal of these materials growing with some arbitrary orientation (with respect to the main temperature gradient) there is a tendency to twin in such a way that the crystal, after twinning, will contain one set of (111) planes more closely coinciding with the main temperature gradient than before twinning. This tendency can be put into action by any slight disturbances in the environment of the growing crystal.

Table I gives the change in orientation, which occurs on twinning, of the various (111) planes for four important orientations of the growing crystal, i.e. [100], [110], [111], and [211]; it demonstrates quantitatively the "advantage" to be gained by such twinning. Fig. 3 (Plate IX) shows a longitudinal cut through a monocrystal of germanium grown along the [100] direction, where all four {111} planes include an angle of $35^{\circ} 16'$ with the growth direction, i.e. the main temperature gradient. After twinning about any one of these planes, there are two sets of densest planes which are only $11^{\circ} 06'$ off the temperature gradient. Of the four growth directions

tabled, [100] would, on this score alone, appear to be the most prone to twinning.

TABLE I.—Changes in Orientation of (111) Planes for Different Orientations of Growing Crystal.

Growth Direction D	No. of (111) Planes	Their Angle with D	D After Twinning Across This Plane	No. of (111) Planes in Twin	Their Angle with D
[100]	4	$35^{\circ} 16'$	[221]	2	$11^{\circ} 06'$
				1	$35^{\circ} 16'$
				1	$74^{\circ} 12'$
[110]	2	0°	[110]	2	0°
				2	$54^{\circ} 44'$
	2	$54^{\circ} 44'$	[411]	1	$15^{\circ} 48'$
[111]	1	$90^{\circ} 00'$	[111]	2	$33^{\circ} 00'$
				1	$54^{\circ} 44'$
	3	$19^{\circ} 28'$	[511]	1	$19^{\circ} 28'$
				2	$33^{\circ} 45'$
				1	$51^{\circ} 06'$
[211]	1	0°	[211]	1	0°
				2	$28^{\circ} 08'$
				1	$70^{\circ} 32'$
	1	$70^{\circ} 32'$	[552]	1	$6^{\circ} 23'$
				1	$22^{\circ} 54'$
				1	$46^{\circ} 13'$
	2	$28^{\circ} 08'$	[721]	1	$70^{\circ} 32'$
				1	$18^{\circ} 18'$
				1	$28^{\circ} 08'$
				1	$38^{\circ} 54'$
				1	$51^{\circ} 49'$

2. INITIATION OF TWINNING

A closer investigation of several mainly cylindrical ingots of germanium and silicon pulled from the melt showed that most twins start from a point where the liquid/solid interface, i.e. the growth front, meets the surface, very often directly from the seed. They usually persist across the whole width of the ingot until the twin plane emerges at the far side (Fig. 3), or alternatively meets another grain or twin boundary (Figs. 2 and 4, Plate IX). Grains twinned about a vertical, or nearly vertical, (111) plane persist throughout the whole length of the ingot (see Fig. 2), whilst any other grains come to an end, sooner or later, if the ingot is long enough. This again is in agreement with the above observation that grains continue to grow preferentially along the (111) planes.

Some of the frequently observed twin bands might be caused by local disturbances, such as the presence of foreign particles. Such particles may appear anywhere on the growing front, and a twin lamella can thus start within the ingot. As soon as the advancing front has left the disturbance behind, the crystal will revert back to its original growth orientation if this

* This has been reported by W. C. Ellis (*Trans. Amer. Inst. Min. Met. Eng.*, 1950, **188**, 886) and confirmed in the present

author's laboratory by R. G. Rhodes and P. J. Holmes, using standard X-ray techniques.

is more favourable, forming a thin twin band which will go on growing across the ingot until it meets the surface again. Fig. 5 (Plate X) shows part of a silicon ingot in section. The main growth was along the [211] direction, and twinning occurred about the (111) plane at $28^{\circ} 08'$ into a [721] orientation (see Table I), in which the most favourable (111) plane was still $18^{\circ} 18'$ off the vertical. After having formed a twin lamella less than a millimetre thick, growth reverted back to the original [211] direction, where there were two vertical (111) planes available.

3. INITIATION OF TWINNING FROM "SHOULDER" OF INGOT

Regarding the detailed mechanism by which twinning is initiated, the silicon ingot shown in Fig. 6 (Plate X) is of interest. This shows in plan a "shoulder"* of (a segment of) an ingot displaying certain growth rings on its surface. These rings are caused by slight deviation in the temperature of the melt from perfect radial symmetry: as the ingot is rotated in the melt about its vertical axis, so growth is enhanced on that part of the ingot which is on the cooler side of the melt, and delayed on the hotter side. The rings form a permanent record of the outline of the ingot during growth; they indicate that this particular ingot—grown from a seed orientated with its [321] direction nearly vertical—tended to assume a polygonal cross-section at a certain stage during growth, the sides of the polygon corresponding with the lines of intersection of the close-packed {111} planes with the surface of the melt. At that stage, a twin lamella had formed at *A*, where conditions for its formation appear to have been particularly favourable: the solid/liquid interface on that side was bounded over a fairly extensive length, >5 mm., by an incipient (111) plane. When, at that stage, growth was temporarily halted by the temperature fluctuations discussed above, to be resumed shortly afterwards, twinning with the new orientation could start simultaneously over that whole length, i.e. as a co-operative phenomenon. It is thus apparent that conditions are much more conducive to twinning from the shoulder than they are on the cylindrical part of the ingot, where twinning usually has to start from a single point, the apex of the ellipse formed by the intersection of the twinning plane with the cylinder. In the particular ingot shown, twinning occurred about the (111) plane, which was 18° off the vertical, and thereby changed the orientation of the other three (111) planes in a way which on balance was rather unfavourable, in the sense discussed above. After growing to a thickness of about 0.7 mm. the twin lamella reverted back to the original orientation by the same process (at *B*). Soon afterwards, the ingot lost its polygonal shape and no further twinning occurred along that side of the shoulder. On the other half of this ingot (not shown in the figure) twinning had

occurred earlier at the shoulder along another side of the polygon; in this case, however, the twin plane was nearly vertical; there was very little change in the orientation of the various (111) planes with regard to the vertical before and after twinning, and therefore no inducement for the crystal to change back to its original orientation. Twinning was permanent and no lamella was formed.

4. INITIATION FROM CYLINDRICAL SURFACE

Twinning occasionally also starts from the cylindrical part of a pulled ingot. When the ingot is grown under steady conditions, i.e. with very uniform diameter, it usually remains monocrystalline, unless and until the temperature suddenly changes. Even a relatively small change in temperature, and hence in growth rate, lasting for a very short time—as judged by the ensuing unevenness of the ingot in the form of a slight bulge or constriction, as the case may be—seems to be sufficient to start twinning from this region. Very sharp temperature gradients—several hundred $^{\circ}\text{C./cm.}$ —exist at the interface between liquid and solid, and the thermal contraction of the ingot as it is withdrawn from the melt can cause considerable stresses, especially if the temperature fluctuates in an uncontrolled manner. The individual atoms making up the ingot will not, in general, be able to take up instantaneously their new equilibrium positions which would correspond to the changing temperature distribution; the deviations of the actual interatomic distances at any particular point from their equilibrium values, which correspond to the instantaneous local temperature, will set up a stress pattern in the crystal, the details of which largely depend on the particular arrangement used. The order of magnitude of these stresses, $\alpha E \Delta T$, where α = linear expansion coefficient, E = modulus of elasticity, and ΔT = temperature change, is comparable with the low strength of the material near the melting point.

5. ATOMIC MISFIT AT INTERSECTION OF TWO TWIN PLANES

An interesting situation arises at the intersection of two twin planes, as, for instance, in the ingot illustrated in Fig. 2. In this case, growth took place along the [211] direction with a vertical twin plane (*A*) separating the left and right halves, I and II, respectively. By the time the front of the growing ingot had reached point *B*, further twinning occurred from the surface; the twin plane (*B*) separating crystal regions II and III then progressed inward—at an angle of $70^{\circ} 32'$ to the vertical—until it met the original twin plane intersecting it along a horizontal line whose crystallographic direction was [110]. The texture of the ingot grown so far was perfect, apart from the stacking faults inherent in the two twin planes *A* and

* I.e. the top part of the ingot where it widens from a thin seed to its final diameter.

B. However, along their intersection perfect fit of the three lattice regions I, II, and III becomes impossible and, as a result of the ensuing strain, further twinning started (region IV). This is illustrated on an atomic scale in Fig. 7, which shows a cross-section of the ingot perpendicular to the line of intersection. The

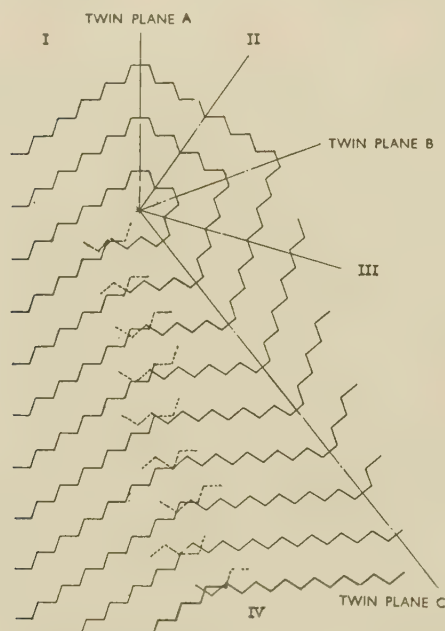


FIG. 7.—Illustrating Lattice Misfit Caused by Multiple Twinning in a [211] Silicon Ingot (as shown in Fig. 2, Plate IX). The chains connect nearest-neighbour atoms lying in the (110) plane common to all four twins, I, II, III, and IV.

crystallographic orientation of this line—and of the cross-sectional plane—is identical for all four crystal regions, [110]. Individual atoms lying in this plane are shown, nearest neighbours being joined by covalent bonds to form chains which run along the various $\langle 110 \rangle$ directions in the different crystal regions. The amount of misfit along the interface, where the third-order twins I and IV meet, is clearly illustrated.

The boundary surface *D* (Fig. 2) between I and IV is thus not a coherent twin plane, but a grain boundary and involves considerable strain energy. Its magnitude corresponds to the elastic energy required to distort the individual chains until they meet their opposite number in the other grain. Laue photographs taken near this boundary displayed reflected X-ray spots which were considerably distorted.

When further twinning started at *E*, further down from the cylindrical surface of the ingot, the intersection of the new twin plane with the grain boundary *D* led to serious fragmentation, followed by a region of large-scale polycrystallinity of the ingot, starting from this line, *F*.

The same type of twinning was observed in almost every silicon crystal grown along a [211] direction, and containing a vertical twin plane, with all details recurring quite regularly and almost precisely as described above.

6. ABSENCE OF GROWTH TWINS IN PULLED METAL INGOTS

Experiments similar to those mentioned before, which established that growth in the cubic structures of low co-ordination number proceeds mainly by an extension of (111) lattice planes, were carried out on copper and aluminium, but revealed no signs of a similar growth mechanism. Owing to the different nature of the metallic bond, there is little, if any, tendency in these face-centred cubic metals, as there is in the structures discussed above, to develop preferentially such (111) planes, which are held together by strongly directed covalent bonds. The mechanism of growth twins outlined above does not, therefore, apply, and growth twins occur but rarely in these metals.

ACKNOWLEDGEMENTS

The author is grateful to Mr. P. J. Holmes for establishing the crystal orientations and some of the numerical values given in Table I, and to Dr. T. E. Allibone, F.R.S., for permission to publish this paper.

TWINNING AND UNTWINNING IN POLYCRYSTALLINE MAGNESIUM*

1566

By R. L. WOOLLEY,† M.A., Ph.D., A.Inst.P., MEMBER

SYNOPSIS

Some aspects of the stress/strain curve of polycrystalline pure magnesium in shear have been studied for cycles of strain-amplitude less than 10%. A qualitative explanation in terms of twinning and untwining processes is given, and is supported by the results of microscopic observation. Special attention is paid to the magnitude of the Bauschinger effect, and also to a characteristic "step" which appears in the stress/strain curve when the material is taken through a cycle consisting of a strain of the order of 10%, followed by a strain in the reverse direction and then a further larger strain in the original direction.

I.—RELATION OF STRESS/STRAIN CURVES TO TWINNING

It is well known that metals which deform by twinning exhibit a large Bauschinger effect (see, e.g., work by Schmidt *et al.*¹). In the course of a study of this effect in polycrystalline pure magnesium, the stress/strain curves shown in Fig. 1 were obtained. These represent shear stress and shear strain in a torsion test, using a tubular specimen 1.27 cm. long,

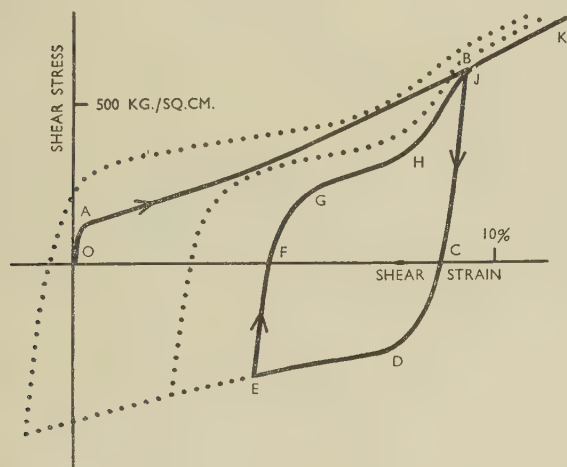


FIG. 1.—Stress/Strain Curve for Polycrystalline Pure Magnesium.

of 1.59 cm. outside dia., and wall thickness 0.16 cm., as described elsewhere.² The specimens were machined from extruded rod of 99.98% purity, kindly supplied by Magnesium Elektron, Ltd., and were annealed at 300°C. for 8 hr. The curve *OABC...K* shows the strain produced by the application and removal of a load of 610 kg./cm.², followed by a load of 366 kg./cm.² in the opposite direction, and then by a load of 732 kg./cm.² in the original direction. The yield stress at *D* is seen to be low compared with the stress at *B*, and the rate of work-hardening along *DE*

is less than along *AB*; there is also a noticeable step in the curve at *HJ*. The two dotted curves, representing specimens tested at reverse stresses of 427 and 549 kg./cm.², respectively, show similar features.

These curves are quite unlike those obtained with cubic metals.² Their general character is, however, qualitatively explicable in terms of twinning and untwining. Such a mechanism has been used to explain the lowering of yield stress in roller-levelled magnesium alloy sheet.³ According to Taylor,⁴ at least five independent shear systems are necessary in each grain of an aggregate if all the grains are to deform with a strain equal to the overall strain of the specimen. This is easily satisfied in face-centred cubic metals, where there are eight independent slip systems of the type (111) $[1\bar{1}0]$. In magnesium at room temperature there are only two independent slip systems, both in the basal plane. (The third basal slip system can be expressed as a linear combination of the other two, and so is not independent.) Besides these there are the six twinning systems; these however, are polar, i.e. if a given twinning system operates when a compression stress is applied in a given direction, this same system would be completely inoperative if a tension stress had been applied in the given direction.⁵ Any twin lamella formed during application of the compressive stress could, however, be untwinned by a subsequent tensile stress in that direction. Thus, in grains favourably oriented with respect to the applied stress, twinning is possible on several planes and Taylor's criterion can be satisfied. It can be shown that these grains are relatively soft. For grains of unfavourable orientation there are less than five shear systems operative, and these grains are relatively hard.

In Fig. 1, along *AB* the grains may thus be crudely classed into two groups: those which are favourably oriented, denoted by *S*, and those unfavourably oriented, denoted by *T*. Along *DE* the stress is reversed, and twinning can occur in the grains *T* and untwining in *S*, so that here all the grains can

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deform easily, producing a low yield stress (D) and a smaller rate of work-hardening (DE). If now a stress is applied in the original direction, grains **S** retwin and grains **T** untwin, so that plastic deformation is still easy (GH). The untwinning of grains **T** is, however, a limited process, which must end when the strain GH is approximately equal to the strain DE . The grains **T** are now back in their original condition as at B , and are unable to deform further in the original direction of strain by twinning. At the point H the specimen changes fairly abruptly from a condition in which all the grains are soft to a condition in which only the grains **S** are soft, exactly as it was at B . The stress/strain curve therefore rises sharply from H to J and continues along JK in prolongation of the curve AB . If all the grains **T** finish untwinning at the same instant, then the slope of HJ would be that of the elastic modulus. The slope is in fact lower than the elastic modulus, presumably because all the **T** grains do not finish untwinning at exactly the same instant. Thus, in Fig. 1, H is the point at which the first **T** grain finishes untwinning, and the point J is where the last **T** grain finishes untwinning.

It might be expected that a step similar to HJ would appear at some point L on DE produced, at the point where the grains **S** are completely untwinned. The strain DL must exceed the strain AB , so L must lie to the left of O . No such step is actually observed, however. In Fig. 1 it can be seen that the step HJ becomes less prominent, the larger the strain-amplitude of the cycle through which the specimen has been taken after B . This is presumably due to work-hardening. It is suggested that during the large strain DL the overall work-hardening greatly reduces the size of the step anticipated at L . Besides this, it is to be expected that the ending of the untwinning of the **S** grains will be spread over a wide range of strain, so that the step, if any, on DE produced, would in any case appear merely as a gradual undulation.

II.—MICROSCOPIC EVIDENCE

Support for this explanation has been obtained by microscopy. If the twinning shear direction in a given grain intersects the free surface, then the surface of the mechanically twinned portion will be tilted relative to the original surface. The specimen is observed with vertical illumination using a microscope objective of not too large an aperture, in this case 16 mm., N.A. 0.28. Because the surface of the twin lamella is not normal to the incident light, only part of the light reflected from it re-enters the objective, so that the twin shows up as darker than its surroundings. One annealed specimen was mechanically

polished and taken through a cycle similar to that of Fig. 1, but of smaller amplitude. Selected areas to a total of about 12 mm.² were inspected and photographed initially and after unloading from B , E , J , and K , and the appearance and disappearance of twin lamellæ noted. The specimen was etched with 2% nitric acid in ethyl alcohol immediately after unloading from B , but not etched after further deformation. Thus the boundaries of mechanical twins formed during the strain AB persist as lines on the specimen surface throughout the remaining deformation. Figs. 2 and 3 (Plate XI) illustrate typical results from two selected areas. These photomicrographs were taken with the material under zero external stress, after unloading from B , E , J , and K , respectively, AB , DE , and JK being 5, 4, and 4%. Fig. 2*B* shows twin lamellæ (dark) in two grains. These lamellæ are reduced in width (partly untwinned) in Fig. 2*E*, where the etched boundaries of Fig. 2*B* are still to be seen. In Fig. 2*J* they have retwinned, and reproduce the appearance of Fig. 2*B*. In Fig. 2*K* some of the original lamellæ have broadened, and further twin lamellæ appear. This behaviour shows that these grains are of type **S**. Fig. 3 shows a corresponding sequence in a grain of type **T**. The twin appears during the strain DE and disappears during FJ ; there are no lines in Figs. 3*J* and 3*K* marking the edges of the twin lamellæ of Fig. 3*E*, because the specimen was not etched at E after the twin was formed. In these photomicrographs the parallel striations in the horizontal direction are due to the fact that, owing to the shape of the specimen, all grinding and polishing had to be carried out in the same direction.

It is difficult to make any quantitative deductions from the microscopic observations, as the only twinning and untwinning observable by this method is in grains lying in the free surface and where the twinning shear produces a substantial surface tilt. The area studied covered roughly 1000 grains. About 100 grains showed twin lamellæ at B identifiable by surface tilts. Of these, more than half showed subsequent untwinning and retwinning as in Fig. 2. Similar numbers showed twinning and untwinning as in Fig. 3.

REFERENCES

1. W. Schmidt *et al.*, *Z. Metallkunde*, 1933, **25**, 229.
2. R. L. Woolley, *Phil. Mag.*, 1953, [vii], **44**, 597.
3. E. A. Calnan and A. E. L. Tate, *J. Inst. Metals*, 1951, **79**, 455.
4. G. I. Taylor, *ibid.*, 1938, **62**, 307.
5. E. Schmid and W. Boas, "Plasticity of Crystals", p. 96. 1950: London (F. A. Hughes and Co., Ltd.).

THE VISCOSITY OF COPPER AND SOME BINARY COPPER ALLOYS*

1567

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SYNOPSIS

The apparatus which had previously been used to determine the viscosity of aluminium alloys (*J. Inst. Metals*, 1952-53, **81**, 145) was modified to deal with the increased temperatures necessary and the higher density of copper and its alloys. The results obtained on copper and certain binary copper alloys show that the viscosity/temperature curves all exhibit an inflection near the liquidus. Above this inflection, the viscosity decreases linearly with increase in temperature; below it the viscosity increases rapidly with decrease in temperature, the curve becoming almost vertical just above the liquidus. For the binary alloys, the viscosity varies in accordance with the equilibrium diagram, there being a maximum at the limit of solid solubility and a minimum at the eutectic.

I.—INTRODUCTION

THIS paper describes an extension of the work on the viscosity of aluminium and binary aluminium alloys¹ in which an apparatus based on the outer-rotating-cylinder method was used. This method has been criticized by Gebhardt, Becker, and Dörner,² whose investigations on aluminium-zinc alloys gave very different results. These authors state that the discrepancy is due to the presence of impurities, particularly oxide, causing a skin effect which increases the value for viscosity. Precautions had, however, been taken in the present authors' work to remove oxygen from the inert gas used, generally nitrogen, by passing the gas through a purification train which included molten aluminium and/or molten sodium. The gas was tested periodically by passing it over a heated small, polished strip of pure copper. The furnace was always under a positive pressure. Whenever the furnace has had to be repaired (such as by patching the refractory lining), special care has been taken to ensure that all moisture has been expelled by long-continued heating. The method used by the German workers does not involve immersion and trouble from the skin effect does not arise. The difference between the two sets of results is due probably to the different methods, and to the possibility that true viscosity is not being measured.

In order to carry out viscosity determinations on copper and its alloys, the original apparatus which had been used with the aluminium alloys required (a) adjustment of the weight of the inner cylinder to counteract the increased buoyancy due to the higher density of copper alloys, and (b) the construction of a new furnace, with suitable insulation and water-cooling, capable of operation at a maximum temperature of at least 1250° C.

II.—MODIFICATION OF THE VISCOMETER

The internal dimensions of the inner cylinder were suitably altered to accommodate a tungsten weight, its mass and displacement being such as to give the required tension in the suspension wire and stability when immersed in molten copper. To withstand the increased operating temperatures, the connecting rod between the inner cylinder and the suspension system was of Inconel for temperatures up to 1150° C. and of Nimonic 90 for higher temperatures.

The new furnace (Fig. 1) embodies:

(1) A liner of 8 in. internal dia. built up of specially made interlocking refractory segments, giving on the inside a continuous spiral groove at a pitch of $\frac{3}{4}$ in. This groove, which has a coating of white fused alumina cement, carries a $\frac{3}{8}$ -in.-dia. spiral of Kanthal A wire. (Adjustment of the pitch of this spiral enables compensation to be made for heat losses at the ends of the winding.) The winding covers approximately 16 in. of the liner and is made up of two sections with a centre tapping. The top section is of 16 S.W.G. wire and the bottom of 14 S.W.G. wire. This difference of gauge was found to be necessary to eliminate temperature differences along the length of the coaxial cylinder system.

(2) Heat insulation, obtained by inserting white crystalline alumina, $\frac{1}{2}$ in. thick, between the liner and a 12-in.-dia. lining of shaped insulating refractory bricks, 2 in. wide. Between this insulating cylinder and the steel casing (21 in. dia.) is a packing of insulating powder.

(3) A water-cooling system consisting of a flat spiral of $\frac{3}{4}$ -in. copper pipe covering the base of the furnace and a vertical spiral of $\frac{3}{4}$ -in. piping at a pitch of $1\frac{1}{2}$ in. along the height of, and in contact with, the furnace casing of mild steel.

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(4) A water-jacketed lid. To protect the spindle bearings and mercury seal of the turntable, an additional water-cooling system is provided by using

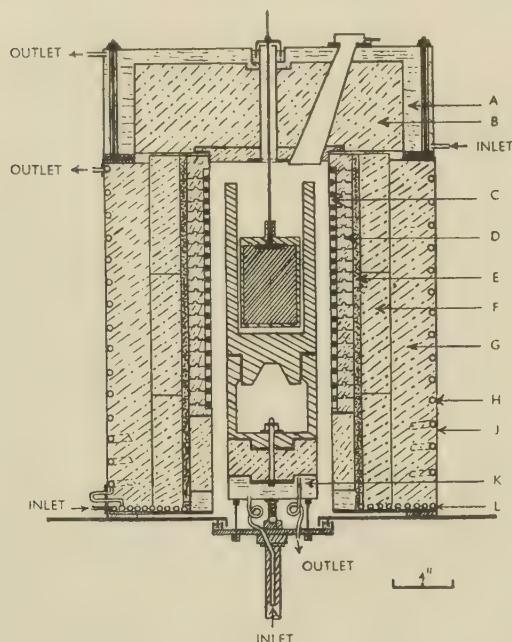


FIG. 1.—Viscometer Furnace and Cooling Systems.

KEY.

- A Water-cooling jacket.
- B Heat insulation.
- C Spiralled coil of Kanthal A wire.
- D Refractory segments.
- E Fused crystalline alumina.
- F Refractory insulating bricks.
- G " powder.
- H Water-cooling spiral.
- J Mild-steel casing.
- K Water-cooled base.
- L Water-cooling system for furnace base.

the spindle as an inlet pipe leading through the turntable to a steel cylinder which acts as the base of the rotating system. The outlet is taken through the turntable to collecting troughs. The rotating system now consists of the cylindrical graphite crucible upon a graphite stand, locking into a heat-insulating brick which fits on to the water-cooled cylinder.

III.—EXPERIMENTAL PROCEDURE

The materials used were electrolytic copper (99.9%), high-purity aluminium (99.9%), "Chempur" tin (99.99%), and silicon of more than 95–96% purity.* Samples for chemical analysis were taken from the top and bottom of a melt by means of a specially made electrode carbon "thief". The composition of each melt is marked on the viscosity/temperature curves. Temperatures were measured with a rare-

* The materials were of the best grade obtainable and the purity quoted is that found in the batch analysis, which was checked if necessary, e.g. the aluminium (the same as that used in the previous work ¹) had the following impurities (as

metal couple, protected by a thin carbon sheath, immersed in the melt, and used with a potentiometer.

A preliminary series of tests was carried out to ensure that the apparatus was working satisfactorily and that there was a condition of "non-slip" between the liquid metal and the cylinder material.

1. THE VISCOSITY OF COPPER

Determinations were carried out to obtain a full viscosity/temperature curve for electrolytic copper from the melting point up to 1250° C. This curve, shown in Fig. 2, was obtained from two different samples of the same composition, using two suspension wires of different characteristics.

The curve is divisible into two sections: (i) in the first there is a gradual increase in viscosity with decrease in temperature up to 10°–15° C. above the melting point, and then (ii) near the melting point the viscosity increases rapidly with decrease in temperature until the curve is almost vertical. Unlike aluminium and its alloys, copper shows no horizontal section, i.e. constant viscosity with temperature variation, up to the maximum temperatures used.

2. THE VISCOSITY OF SOME BINARY COPPER ALLOYS

The viscosity of binary alloys of the following compositions have been determined: silicon 0.8%; aluminium 0.15%; tin 0.35%.

Alloying and sampling were carried out as for the aluminium alloys.¹ No segregation was observed during the experiments. The results are shown in Figs. 3–6.

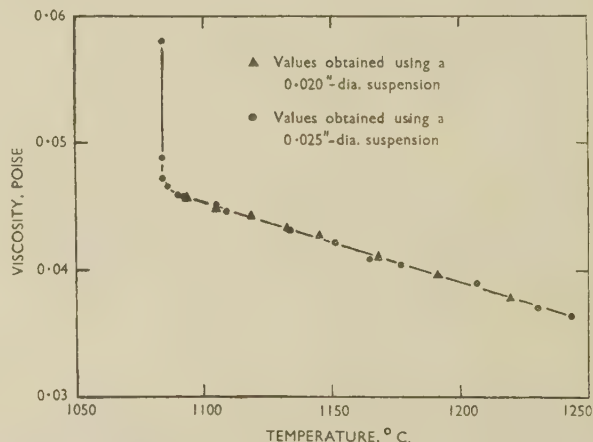


FIG. 2.—Viscosity/Temperature Curve for Electrolytic Copper.

A few determinations on other binary alloys have also been made, e.g. those containing additions of "Mond" nickel up to 3% and electrolytic manganese up to 4½%.

determined): iron 0.01%; silicon 0.01%; manganese 0.003%; nickel <0.001%; chromium <0.001%; calcium <0.001%; magnesium <0.001%; copper 0.001%.

suitable for determining the viscosity/temperature relationship of copper-zinc alloys owing to the fact that the loss of zinc at the high temperatures alters the composition of the alloys. The curves obtained in trial melts, however, were similar in shape to those of the other alloys.

IV.—EXPERIMENTAL RESULTS

1. THE VARIATION OF VISCOSITY WITH TEMPERATURE

Copper and the binary alloys tested give the same type of curve, exhibiting a linear increase in viscosity

as the liquidus is approached, and (c) the actual viscosity, with a certain dependence on the constitution.

(a) Copper-Silicon Alloys

The addition of silicon to copper (Fig. 3) causes a slight increase in slope over the range 0–5.25%, with a much greater increase when this range is exceeded, i.e. the 6.2 and 7.34% alloys. The rate of change of slope varies similarly, being over a range of 15°–20° C. in the α region and 25°–30° C. for compositions beyond that. The variation of viscosity with composition at 50° C. above the liquidus is shown in Fig. 3 (inset). There is a gradual increase in viscosity with increase

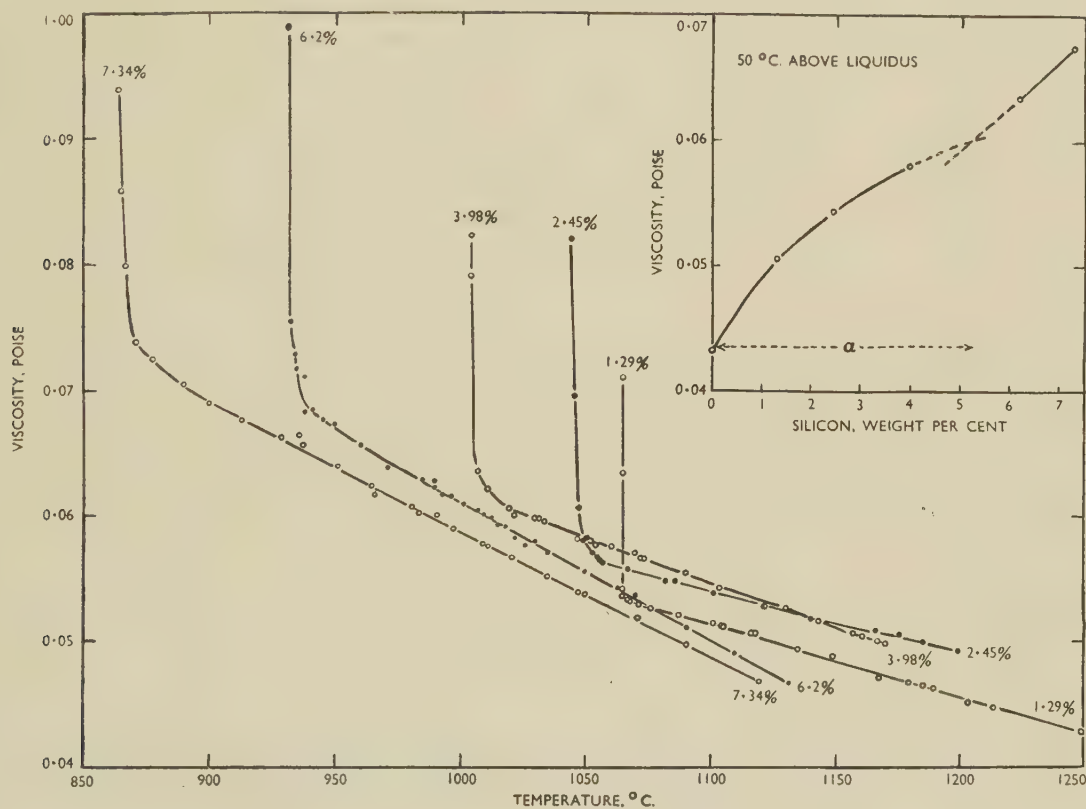


Fig. 3.—Viscosity/Temperature Curves for Copper-Silicon Alloys.

with decrease in temperature until the liquidus—or melting point—is approached, when the slope of the curve increases rapidly until it is almost vertical just before solidification begins. Unlike aluminium and its alloys, no second change point at a higher temperature was noticed up to the maximum temperature of test (1250°–1300° C.).

2. THE VARIATION OF THE VISCOSITY/TEMPERATURE CURVE WITH COMPOSITION

As was observed with aluminium alloys, the effect of an alloying element is to alter (a) the rate of change of viscosity with temperature, i.e. the general slope of the curve, (b) the rate at which the slope increases

in silicon in the α range, with a greater rate of increase beyond that range.

(b) Copper-Aluminium Alloys

The effect of aluminium additions (Fig. 4) is to cause an increase in the slope of the viscosity curve. Above the eutectic composition (8.5% aluminium) there is a greater increase in the slope, the change of slope occurring over 15°–20° C. The variation with composition (Fig. 4, inset) shows a peculiarity beyond the limit of solid solubility (7.5% aluminium). In the α range, there is a gradual increase with aluminium content, with a decrease in viscosity just above the limit of solid solubility. Further additions

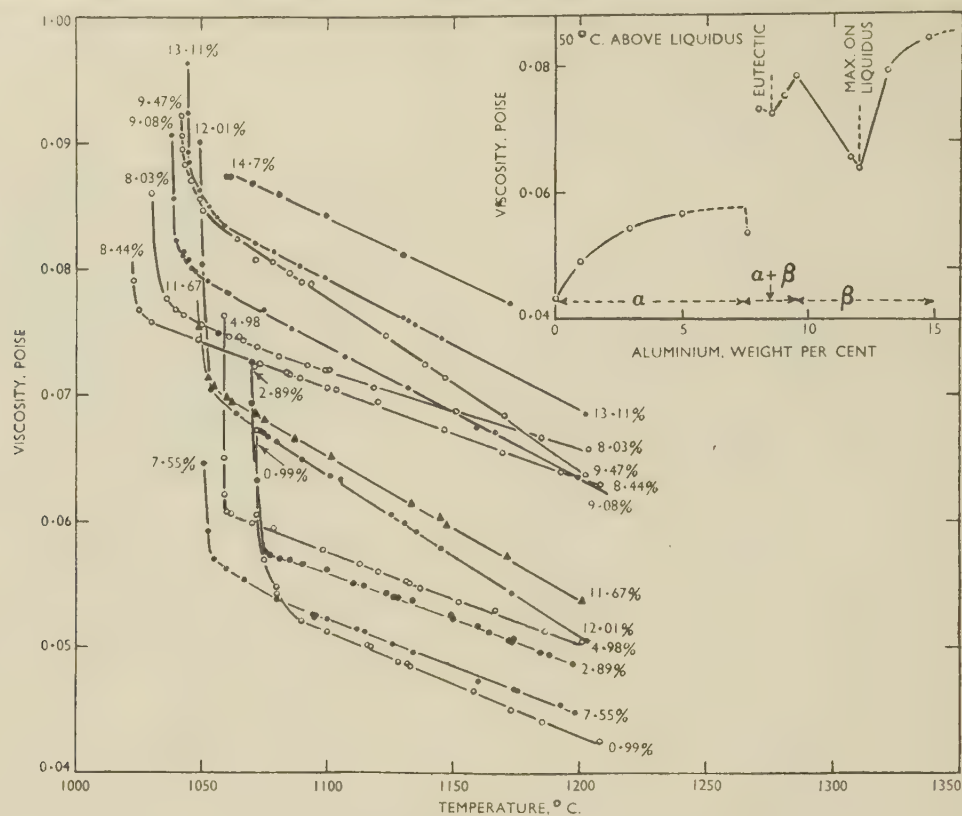
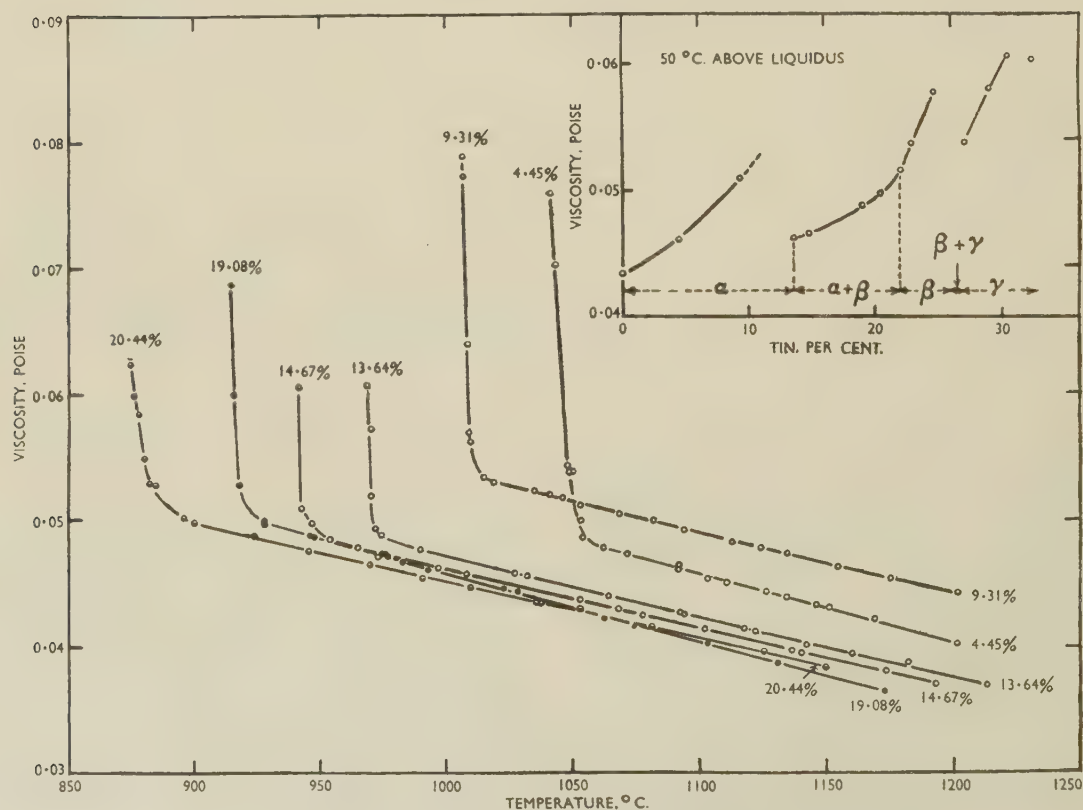


FIG. 4.—Viscosity/Temperature Curves for Copper-Aluminium Alloys.

FIG. 5.—Viscosity/Temperature Curves for Copper-Tin Alloys in $(\alpha + \beta)$ Range.

of aluminium, instead of continuing the decrease, caused a considerable rise in the viscosity in the ($\alpha + \beta$) range. The variation then follows the expected pattern, decreasing to the eutectic composition and increasing to the edge of the wholly β range (9.5% aluminium). Beyond this, the viscosity decreases to a minimum at 12% aluminium, corresponding to the maximum on the liquidus in the β

slope of the viscosity curve, while the change of slope occurs over a range of 15°–20° C. (Fig. 5). Beyond the ($\alpha + \beta$) field, the slope increases, and the change of slope is over a range of 25°–30° C. (Fig. 6). The effect of composition (Fig. 5, inset) upon the viscosity value at 50° C. above the liquidus, is to give an increasing slope of the curve depending on the solid solution present. Each field (α , $\alpha + \beta$,

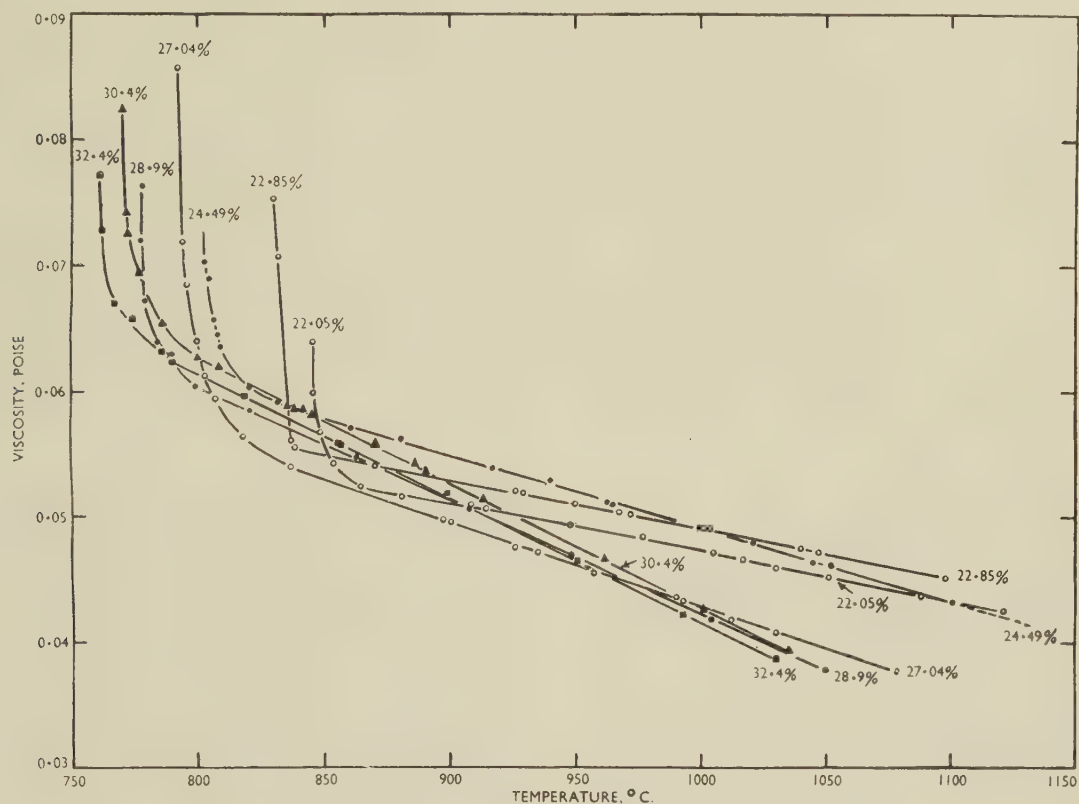


FIG. 6.—Viscosity/Temperature Curves for Copper-Tin Alloys in Higher Range.

range. Then there is an increase in viscosity between 12 and 14.7% aluminium. It should be noted that the positions of the curves for alloys with 8.03 and 8.44% aluminium were checked repeatedly to ensure that they were correct. It is possible that this peculiarity may be due to the fact that the solid solubility of aluminium increases with decrease in temperature, the effect of this increase in solubility overriding the expected decrease in viscosity up to the eutectic composition.

(c) Copper-Tin Alloys

The addition of tin up to the edge of the ($\alpha + \beta$) region (22.0% tin) gives rise to a slight decrease in the

β , &c.) has a characteristic curve apparently discontinuous from the others or intersecting at the phase boundaries.

ACKNOWLEDGEMENT

One of the authors (W. R. D. J.) acknowledges gratefully financial assistance from the Department of Scientific and Industrial Research.

REFERENCES

1. W. R. D. Jones and W. L. Bartlett, *J. Inst. Metals*, 1952–53, **81**, 145.
2. E. Gebhardt, M. Becker, and F. Dörner, *Z. Metallkunde*, 1954, **45**, (2), 83.

1568 THE BAINITIC TRANSFORMATION OF THE BETA PHASE IN COPPER-ZINC ALLOYS *

By R. D. GARWOOD,† M.Sc., MEMBER

SYNOPSIS

The isothermal decomposition of the metastable β phase has been studied in a copper-zinc alloy containing 41.3% zinc over the temperature range 170°–470° C. The plate-like particles precipitated below approximately 350° C. develop by a process of slow, coherent growth, causing surface upheavals analogous to those occurring in the formation of bainite in iron-carbon alloys. Many faint lines in addition to those of the α lattice appear in the X-ray spectra during transformation below 225° C., giving a pattern almost identical with that of low-temperature martensite. In addition, the habit planes adopted during the early stages of decomposition are the same as those reported for the sub-zero martensitic transformation.

It is concluded that the arguments of Ko and Cottrell concerning bainite formation (*J. Iron Steel Inst.*, 1952, **172**, 307) apply with equal force to this system. The plates grow isothermally by the same co-operative movement of atoms as occurs in the martensitic transformation. Continued growth is possible only provided that a change in composition of the precipitate occurs by diffusion, causing relief of strain and an increase in the driving force for transformation.

Above 350° C., simultaneous decomposition occurs by an alternative process which gives particles of irregular shape. At higher temperatures, these develop into ill-defined needles to the exclusion of the regular plates. The absence of relief effects suggests that this high-temperature precipitate is "incoherent" with the β matrix.

I.—INTRODUCTION

BAINITE is a generic term used to describe the acicular transformation products formed during the isothermal decomposition of austenite at temperatures below the "nose" of the time/temperature/transformation diagram. The mode of formation of bainite in iron-carbon alloys has been the subject of much discussion for a number of years. The main difficulty arises from the general practice of classifying phase transformations in solid metals into two types: (i) martensitic transformations, and (ii) nucleation-and-growth transformations. The former occur during cooling by the sudden appearance of fully developed plates, but the reactions cease when the fall of temperature is arrested. Transformations of this type are diffusionless, for crystals of the new phase form too quickly for a change in composition to occur. On the other hand, in the second type of transformation the growth of the new phase is controlled by the thermally activated transfer of atoms, so that decomposition takes place isothermally as well as during cooling.

The slow increase in length and thickness of the needles reported by Smith and Mehl¹ indicates that the bainite reaction is of the latter type. However, the needles of martensite are so similar in external form to those of bainite that the two processes of growth must be related.

This apparent anomaly has been largely resolved by Ko and Cottrell² from the observation of surface-relief effects during the isothermal formation of bainite. They concluded that bainite forms by a shear-type transformation involving a process of slow,

coherent growth. The atom movements are thus essentially the same as those for the formation of martensite, except that the rate of transformation is limited by the removal of carbon from the region of the growing plate. This loss of carbon not only increases the driving force for the transformation but also reduces the strain energy developed in the matrix by the volume change. Carbon depletion can occur either by diffusion into the surrounding austenite or by the precipitation of carbide particles. Presumably, the latter mechanism predominates in plain carbon steels, resulting in a dark-etching, heterogeneous decomposition product. The duplex structure is only a secondary characteristic of the transformation, and where carbon loss takes place by matrix enrichment the plates are light-etching and homogeneous, e.g. the so-called "X" constituent in certain alloy steels.³

From this point of view martensitic transformations in other alloy systems should be accompanied by isothermal reactions of the bainite type provided that: (a) the rate of diffusion permits decomposition within a measurable time, and (b) prior decomposition does not occur by an alternative process of the "incoherent" type. The validity of this argument has been tested in the present work by studying the isothermal decomposition of the metastable β phase in a brass of near 60:40 composition. X-ray, hardness, and microscopical methods have been used to investigate the transformation over the range 170°–470° C.

The related martensitic transformation was first reported by Greninger and Mooradian⁴ in an alloy

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containing 39.21% zinc. After being quenched to retain the β phase, the alloy transforms on cooling to -40°C . into a structure of low and uncertain symmetry. As in iron-carbon alloys, the M_s temperature varies with composition⁵ and occurs above room temperature in an alloy containing 39% zinc + 1% lead and tin.⁶ In this case the product is face-centred tetragonal ($a = 3.75 \text{ \AA}$, $c/a = 1.043$), but reverts to face-centred cubic on tempering. Alloys whose compositions lie within the range of β stability at room temperature do not undergo the martensitic transformation on cooling.⁴

II.—EXPERIMENTAL

1. PREPARATION OF THE ALLOY

The alloy was prepared from electrolytic copper (99.99%) and "Crown Special" zinc (99.99%) and then chill-cast in the form of a slab ingot 0.6 in. thick. This was hot rolled into $\frac{1}{10}$ -in. sheet to provide specimens of suitable dimensions for isothermal transformation. The alloy contained 58.7% copper and 41.3% zinc (by difference).

2. ISOTHERMAL TRANSFORMATION

Small specimens, $\frac{1}{2} \times \frac{1}{4} \times \frac{1}{10}$ in., were solution-treated for 20 min. at 820°C . and then quickly transferred to the isothermal-transformation bath. Below 250°C . this consisted of a nitrite/nitrate salt mixture, but for higher temperatures a more rapid rate of cooling was obtained with a molten alloy of lead and tin. The temperature of the bath was thermostatically controlled to within $\pm 2^\circ\text{C}$. After quenching in water to interrupt transformation, the specimens were sectioned and the surfaces prepared for microscopical examination by electrolytic polishing in 1:1 orthophosphoric acid. In all cases slight decomposition occurred during transfer into the liquid bath, resulting in a fringe of fine α needles at the boundaries of the β grains. It was impossible to suppress this grain-boundary transformation, but the deposit did not play a significant part in the isothermal transformation below 400°C .

Several stages of transformation at 225°C . are shown in Figs. 1-3 (Plate XII), which typify the mode of decomposition at low temperatures. The precipitate first appears as thin plates which increase in length with longer times in the transformation bath. However, the plates thicken only comparatively slowly. Additional particles appear later, and ultimately the interlocking network is so complex that it is difficult to identify the areas of untransformed β in the matrix. During the early stages of decomposition the plates frequently occur in pairs, with an obtuse angle between the two sections.

The change in the form of the precipitate as the transformation temperature is raised is illustrated in Figs. 4-6 (Plate XII), the initial stages of precipitation being shown in each case. Little change is visible at 300°C . (Fig. 4), except that the final

structure is coarser, i.e. the number of plates formed per unit volume has decreased, but above 350°C . (Fig. 5) a significant difference occurs, for a considerable amount of irregular debris is formed in addition to the thin plates observed at lower temperatures. Both the plates and the irregular particles increase in size with longer times at the bath temperature. At 430° (Fig. 6) and 470°C . the particles are again larger and are all of irregular outline at the start of precipitation. Later they develop into ill-defined needles clustered in small groups or colonies. All the needles in a single colony have their axes approximately parallel to each other. At these higher temperatures the α needles precipitated at the β grain boundaries during cooling continue to grow in the isothermal bath and develop into very large

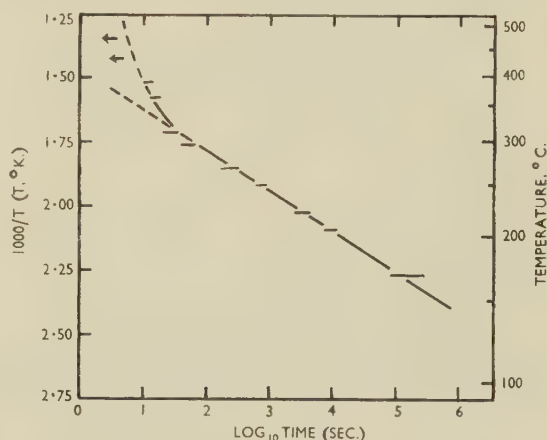


Fig. 9.—Reciprocal Rate Plot of Incubation Period for Isothermal Transformation of Brass Containing 41.3% Zinc.

colonies. For this reason the time at which transformation begins could not be accurately fixed above 400°C .

The fine nature of the precipitate prevented the application of quantitative methods to measure the extent of decomposition. The kinetic studies were therefore limited to an assessment of the incubation period. In Fig. 9 the time at which particles of precipitate first appear is plotted on a logarithmic scale against the reciprocal of the absolute temperature. The graph is a straight line below 315°C ., and the activation energy derived from its slope is 30,000 cal./mole within ± 2000 cal.

3. HARDNESS

The hardness values reported were obtained approximately 12 months after heat-treatment. Impressions taken within a few days of quenching showed wide variation and little correlation with the microstructure. This was attributed to the age-softening of the β phase associated with the order-disorder transformation.^{7,8} The long delay between heat-treatment and hardness testing ensured that this process was complete.

The hardness changes accompanying precipitation are shown in Fig. 10. At the lowest temperatures, e.g. 170° C., transformation is marked by a hardness increase of some 55 D.P.N. As the transformation temperature is raised, the hardness approaches a maximum in a shorter time and this is followed by softening. The value of the maximum hardness reached decreases as the transformation temperature is raised. In all cases the increase in hardness begins at approximately the same time as that at which

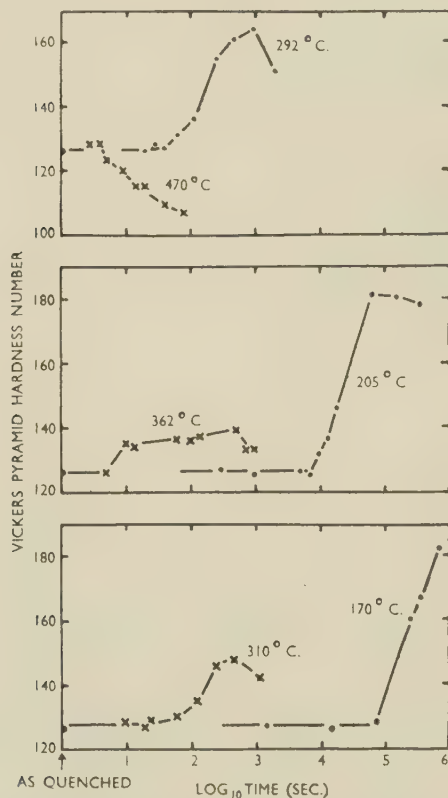


FIG. 10.—Change in Hardness on Isothermal Transformation of Brass Containing 41.3% Zinc, at Temperatures Indicated.

particles of precipitate are first detected within the β grains. At 362° C. there is little change in hardness during transformation, whereas at 470° C. the rapid decomposition gives rise to marked softening.

4. SURFACE-RELIEF EFFECTS

In view of the rapid deterioration of polished surfaces due to the volatilization of zinc at high temperatures, a modification of the heat-treatment procedure was necessary to permit a study of the relief structures produced by transformation. The isothermal-transformation technique was therefore replaced by the more conventional quench-and-temper method. This change should not materially alter the course of transformation, since the M_s point is well below room temperature. The following procedure was adopted: After solution-treatment at

820° C., the specimens were quenched in 10% caustic soda solution. Sectioned surfaces were then prepared by electrolytic polishing, and the specimens were sealed under an atmosphere of dry argon in Pyrex glass capsules. Tempering in a salt bath at various selected temperatures at 50° C. intervals followed and, after cooling, the polished surfaces of the specimens were examined for relief effects.

Changes in surface contour were observed to accompany decomposition on tempering up to 350° C. The nature of the relief obtained is shown in Fig. 7 (Plate XII), for a specimen tempered for 10 min. at 300° C. The β matrix is raised on one side of the plates and correspondingly depressed on the other. In view of the small scale of the relief effect (magnification $\times 1000$), it was difficult to establish the exact contour of the plates. However, a half-tone appearance given by dark-field illumination indicated a slight tilt of the surface between the two different levels of the matrix. At 350° C., the highest temperature at which relief structures were observed, the effect was not clearly marked, for the surface contours were more curved and undulating in character than those produced at lower temperatures. That these changes were caused by the precipitation process and not by some subsidiary thermal-etching effect, was proved by tempering specimens already decomposed by isothermal transformation, when it was found that the polished surfaces were unaffected by the treatment. Comparison of the microstructures of quenched and tempered specimens with those which had been given an equivalent isothermal transformation showed that decomposition occurs more rapidly using the latter technique. The only other significant difference between the two methods of treatment was that the plate-like mode of decomposition persisted to higher temperatures on tempering, before changing to the more irregular, needle form of precipitate.

5. X-RAY EXAMINATION

In view of the difficulties of heat-treating metal powders, the X-ray examination was carried out on small wires taken from the isothermally transformed specimens. These were prepared by cutting thin slivers, $2 \times 2 \times 5$ mm., from the centre of the test-piece with a jeweller's hack-saw. The slivers were deeply etched with nitric acid to a dia. of 0.3–0.5 mm. in order to remove the work-hardened zone. Exposures were made in a 19-cm.-dia. camera, using either Cu or Co filtered radiation.

No unexpected changes in the Debye-Scherrer patterns were observed during transformation at the highest temperatures of the range investigated. The appearance and intensification of the α lines were accompanied by a shift in the high-angle β lines due to the zinc enrichment of the matrix. Both the α and β lines remained relatively sharp during transformation. At lower temperatures, i.e. below 350° C., a diffuse broadening of the β lines accompanied decomposition, so that accurate parameter measurements could not

be made. However, a detectable shift of the β lines occurred at all temperatures.

The most interesting results were obtained below 225° C., when many faint lines appeared during transformation, in addition to those of the α lattice (Fig. 8, Plate XII). A list of the α spacings calculated from these is given in Table I, together with

TABLE I.—New Lines Present in X-Ray Patterns of Metastable β -Brass Isothermally Transformed Below 225° C., Compared with Those Reported in Patterns of Low-Temperature Martensite.

Line	Indices of Equivalent Line in F.c.c. α Lattice $a \sim 3.70$ Å.	Low-Temperature Martensite		Isothermal Transformation Between 170° and 225° C. 41.3% Zn
		Greninger and Mooradian. ⁴ 39.21% Zn	Isaichev and Miretsky. ⁹ 40% Zn	
		Å.	Å.	Å.
a	2.26	2.23 -2.24
b	2.19	...
c	(111)	?	2.13	2.12 -2.13
d	2.04	2.02 -2.04
e	...	1.96	1.96	1.93 -1.935
f	(200)	1.87	1.88	1.84
g	1.73
h	1.61	1.64
i	...	1.33	1.33	...
j	(220)	1.29	1.295	1.297-1.301
k	...	1.24	1.235	1.230
l	...	1.18	...	1.171-1.174
m	...	1.145	1.145	...
n	...	1.132	1.138	...
o	(311)	...	1.118	1.108-1.109
p	...	1.095	1.092	1.093-1.095
q	1.076-1.078
r	(222)	1.068	...	1.062-1.064
s	1.027	...
t	...	0.872
u	...	0.859
v	...	0.853
w	...	0.835

the values reported by Greninger and Mooradian⁴ and Isaichev and Miretsky⁹ for the sub-zero martensitic transformation. Nearly all the new lines appearing on isothermal transformation occur in the pattern of the low-temperature martensite. The slight discrepancies in numerical value may be due to the different compositions of the alloys used. On the other hand, certain lines of the martensite pattern do not appear on isothermal transformation, i.e. lines *i*, *m*, and *n*. The most probable explanation of this difference is to be found in the higher copper content of the isothermal decomposition product, a change indicated by the β line shift.

6. HABIT PLANES OF THE PRECIPITATE

A comprehensive study of the variation of the habit planes of the low-temperature precipitate with the transformation temperature has not been attempted. The determination was confined to a single isothermal heat-treatment, namely 116 min. at 225° C. (Fig. 2, Plate XII). The orientation of the parent β grains was obtained by the Greninger back-reflection Laue

method,¹⁰ and the habit planes of the precipitate were determined stereographically, using the single-surface technique recommended by Bowles.¹¹ The structure of the precipitate is so fine that it was impossible to follow the traces from one surface to another. However, the findings were confirmed by observing traces in a second polished surface and pairing off all possible combinations of trace normals to find the recurring plane. The habit-plane poles were fixed to an accuracy within $\pm 1^\circ$.

It was found that the poles of the β planes delineated by the precipitate plates were not of low indices, but occurred scattered within a region of the unit stereographic triangle bounded by the points (155), (166), and (2,11,12) (Fig. 11). The centre of this area occurs

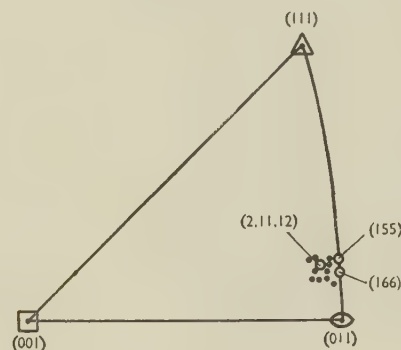


Fig. 11.—Stereographic Projection of Poles of Plates Precipitated during Isothermal Transformation of Metastable β Brass for 116 min. at 225° C.

some 7° from the appropriate pole of the (011) type. The solution is identical with that reported by Greninger and Mooradian for the strain transformation.⁴

The plates occur characteristically grouped in pairs, the two poles of the contiguous plates lying on diametrically opposite sides of the pertinent (011) pole. In view of the small dimensions of the plates and the scatter of the poles over an area, it was not possible to fix the common direction of intersection with great precision. For a pair grouped on each side of the (011) pole, e.g. (2,11,12) and $(\bar{2},12,11)$, this direction lies in the (011) plane between $[0\bar{1}1]$ and $[\bar{1}\bar{2}2]$. When this common direction lies in or near the plane of the polished surface the cross-section of the pair of precipitate plates appears under the microscope as a single, thin needle. At other orientations with respect to the polished surface the characteristic V formation is observed.

III.—DISCUSSION

Although the surface-relief effects are not so well defined as in iron-carbon alloys, there can be no doubt that the arguments of Ko and Cottrell² concerning bainite formation apply equally well to the plate-like precipitates formed by the isothermal transformation of β -brass below 350° C. The preferred habit planes

of the isothermal precipitate at 225° C. are the same as those reported for the martensitic transformation,⁴ and the many additional lines appearing in the Debye-Scherrer patterns below this level are almost identical with those obtained on sub-zero cooling.

These three related observations provide strong evidence that nuclei grow isothermally by the same co-operative movement of atoms as is responsible for the martensitic transformation. The raising and lowering of the β matrix on alternative sides of the plates is an indication that coherency exists between the two lattices. The resulting localized strain within the β lattice, a strain evidenced by the β line broadening accompanying transformation, is probably the main reason for the observed hardness rise of 55 D.P.N. at low transformation temperatures. In other precipitating systems where hardening has been attributed to coherency, the rise of hardness frequently occurs before precipitation is visible under an optical microscope. The fact that visible precipitation and hardening are in this case in step may be due to the small change in specific volume and a lower rate of nucleation. A large number of intense strain centres will exert a greater influence on the macro-hardness than a comparatively small number of larger particles. For the same reason, the hardness change is not so great at higher transformation temperatures where the rate of nucleation is lower. This is not the only factor, however, for stress-relief by some process similar to recovery will occur to a greater extent as the transformation temperature is raised. Secondary processes of this type may be responsible for the more undulating appearance of the relief structures at 350° C.

This qualitative picture is not complete, however, for at 360° C. (Fig. 5, Plate XII) an alternative mode of decomposition is observed. At this temperature transformation proceeds by the simultaneous growth of the V-shaped pairs of plates and of much more irregular particles. The former mode of decomposition ceases to operate as the temperature is raised, transformation occurring wholly by the formation of the irregular, needle-shaped clusters. These particles are incoherent with the β matrix, for the precipitation is not accompanied by surface-relief effects; the β lines in the X-ray spectra remain sharp throughout transformation and there is a rapid fall in hardness.

When the coherent growth and incoherent growth of nuclei occur simultaneously, i.e. within the approximate range of temperature 350°–400° C., a clear distinction between the two separate growth processes is possible only during the early stages of transformation. The growing plates must break away from the β matrix after exceeding a certain critical size, when their further development will be by an incoherent process. The regularity of their outline is then lost.

In the case of iron-carbon bainite, coherent isothermal growth is possible above the M_s temperature only if carbon is removed from the growing plates.

A similar criterion must apply to the coherent decomposition of β -brass, and since the plates are homogeneous throughout their growth, the necessary composition change is by the zinc enrichment of the matrix. Recently, Landergren and Mehl¹² have reported that the activation energy for diffusion in the β phase is 17,600 cal./mole. This is in good agreement with the value of 15,400 cal./mole obtained in the age-softening studies of Green and Brown.⁸ Assuming that there is no great variation with composition, these figures are well below the 30,000 cal./mole obtained from Fig. 9 for the induction period preceding visible precipitation. The most reasonable explanation of this discrepancy is that diffusion within the precipitate is the main factor limiting growth. In this respect the observed activation energy is of the same order as that for diffusion in α -brass.

Additional lines are detected in the Debye-Scherrer photographs of specimens transformed below 225° C. It is doubtful whether this temperature has any particular significance, and the effect may well be observed at higher temperatures by the use of a more sensitive X-ray technique. The crystal structure from which these lines originate has not yet been determined, but most probably they arise from the regions of the precipitate strained into coherency with the β matrix. Many of the lines in the spectra formed on isothermal decomposition at low temperatures correspond to lines from the face-centred cubic α lattice, and it is unlikely that the pattern represents a single unique structure. This conforms with the suggestion that coherence is lost when the plates exceed a certain critical size.

ACKNOWLEDGEMENT

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REFERENCES

1. G. V. Smith and R. F. Mehl, *Trans. Amer. Inst. Min. Met. Eng.*, 1942, **150**, 211.
2. T. Ko and S. A. Cottrell, *J. Iron Steel Inst.*, 1952, **172**, 307.
3. E. S. Davenport, *Trans. Amer. Soc. Metals*, 1939, **27**, 837.
4. A. B. Greninger and V. G. Mooradian, *Trans. Amer. Inst. Min. Met. Eng.*, 1938, **128**, 337.
5. V. Ganenko and T. Zempur, *Zhur. Tekhn. Fiziki*, 1940, **10**, 571.
6. I. Isaichev, E. Kaminsky, and G. Kurdjumow, *Trans. Amer. Inst. Min. Met. Eng.*, 1938, **128**, 361 (discussion).
7. C. S. Smith, *ibid.*, 1943, **152**, 144.
8. H. Green and N. Brown, *ibid.*, 1953, **197**, 1240.
9. I. Isaichev and V. Miretsky, *Zhur. Tekhn. Fiziki*, 1938, **8**, 1333.
10. A. B. Greninger, *Trans. Amer. Inst. Min. Met. Eng.*, 1935, **117**, 61.
11. J. S. Bowles, *ibid.*, 1951, **191**, 44.
12. U. S. Landergren and R. F. Mehl, *J. Metals*, 1953, **5**, (2), 153.

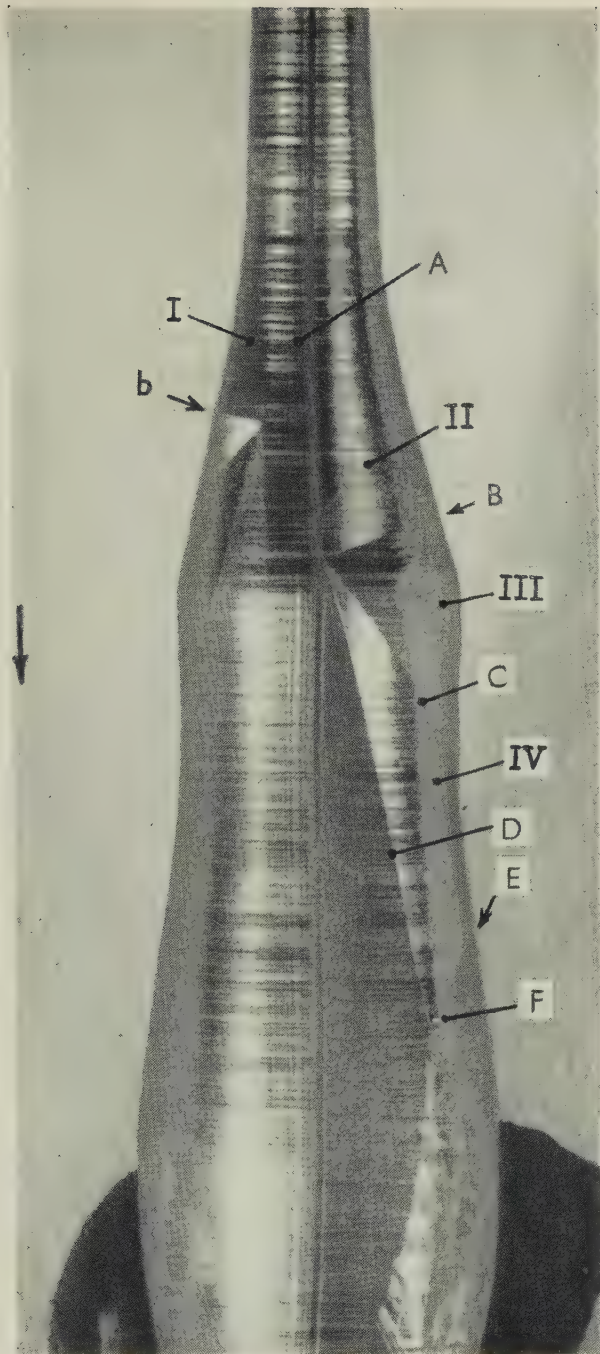


FIG. 2.—Silicon Ingot with Vertical Twin Lamellæ *A* and Further Twinning at *b*, *B*, *C*, and *E*. $\times 5.6$.



FIG. 3.—Twinned Germanium Ingot. $\times 2$.

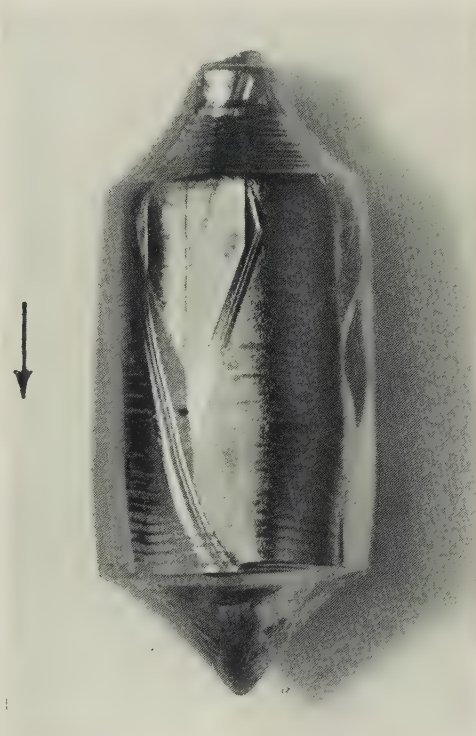


FIG. 4.—Twin Bands in Silicon Ingot. $\times 2$.

Arrows indicate growth direction.

[To face p. 68.]



FIG. 5.—Section of Silicon Ingot
Containing Two Twin Lamellæ,
Starting within the Ingot.
Arrow indicates growth direction.

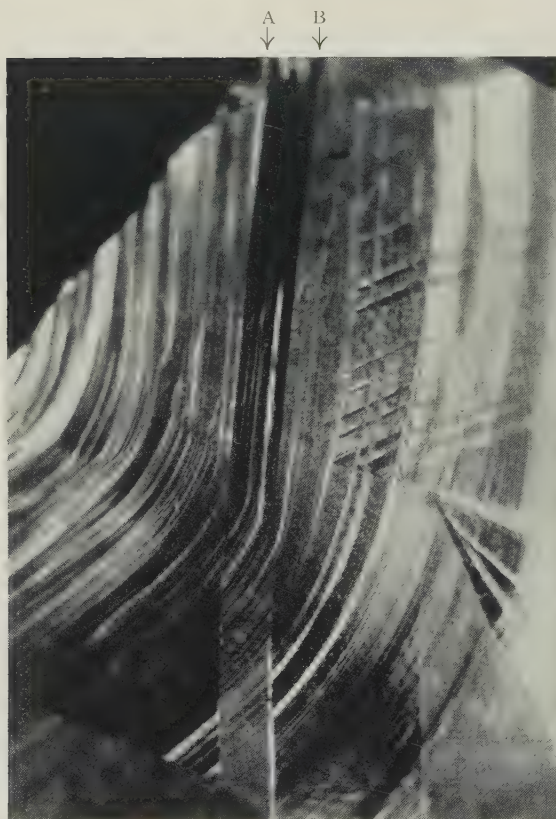


FIG. 6.—Growth Rings and Twin Lamella Between *A* and
B on "Shoulder" of Silicon Ingot. $\times 10$.

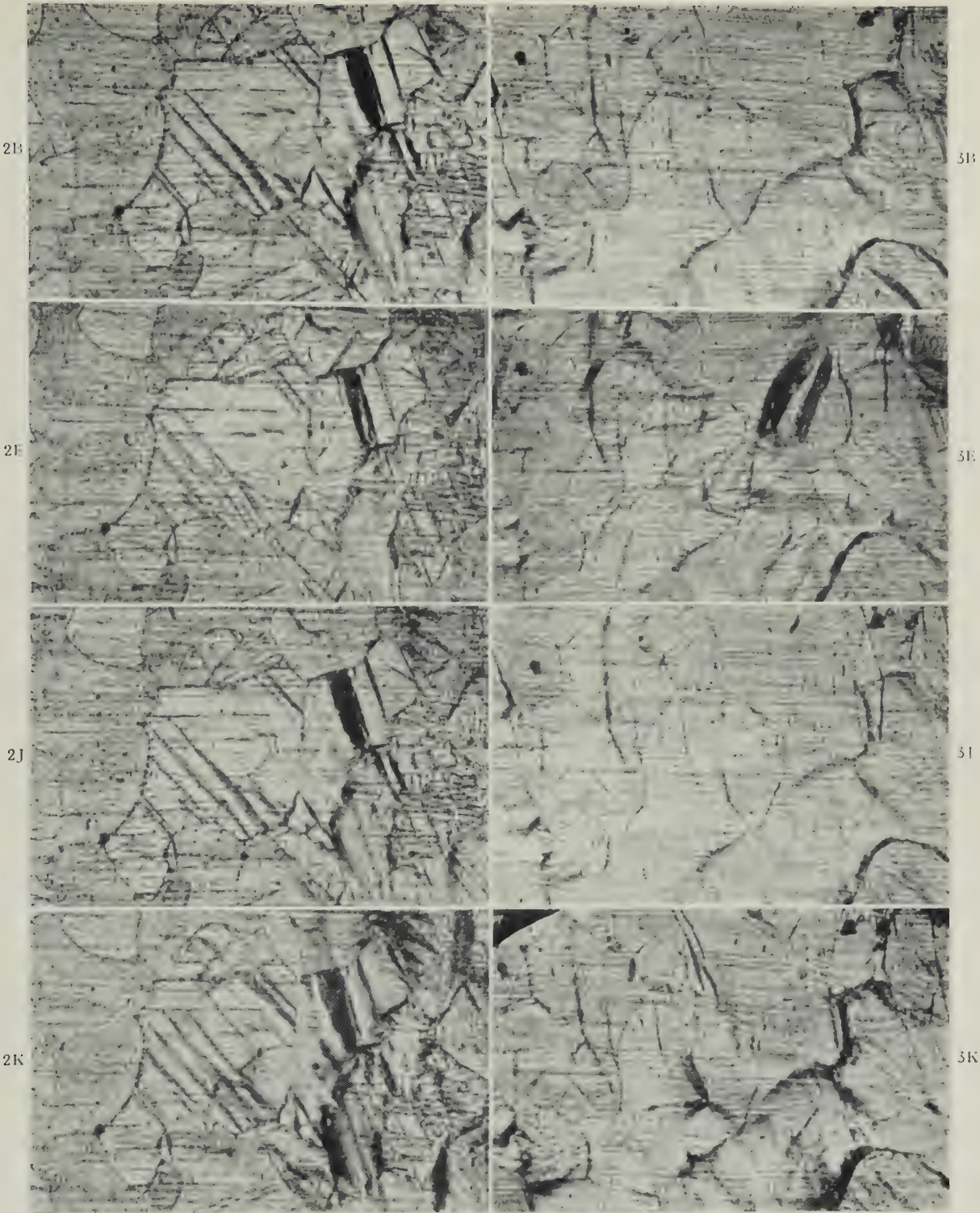


FIG. 2.—Sequence of Twinning, Untwinning, and Retwinning in Polycrystalline Magnesium. Grains of type **S**. $\times 190$.
FIG. 3.—Sequence of Twinning and Untwinning in Polycrystalline Magnesium. Grains of type **T**. $\times 190$.

B, E, J, and K refer to the points in Fig. 1.

MICROSTRUCTURES OF ISOTHERMALLY TRANSFORMED BRASS CONTAINING 41.3% ZINC.



FIG. 1.—60 min. at 225° C. × 1000.
 FIG. 2.—116 min. at 225° C. × 1000.
 FIG. 3.—21½ hr. at 225° C. × 1000.

FIG. 4.—2 min. at 300° C. × 1000.
 FIG. 5.—40 sec. at 360° C. × 500.
 FIG. 6.—16 sec. at 430° C. × 500.

FIGS. 1-6.—Etched in ammoniacal ammonium persulphate.

FIG. 7.—Surface-Relief Structure Produced by Tempering a Quenched Specimen for 10 min. at 300° C. × 1000.

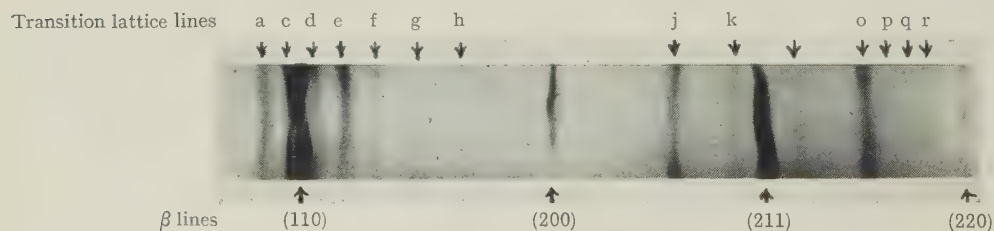


FIG. 8.—Portion of X-Ray-Diffraction Pattern of Brass Containing 41.3% Zinc Isothermally Transformed for 143 hr. at 170° C., Showing Transition-Lattice Lines. $\text{CuK}\alpha$ radiation.

THE CREEP AND FATIGUE PROPERTIES OF SOME 1569 WROUGHT COMPLEX ALUMINIUM BRONZES*

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(Communication from The British Non-Ferrous Metals Research Association.)

SYNOPSIS

Creep tests at 300° and 400° C. on complex aluminium bronzes containing 5% each of iron and nickel, with aluminium contents from 0 to 11.6%, indicate that alloys with 3–7% aluminium have the best creep properties. These are relatively difficult to forge, and the best combination of creep properties with ease of forging is given by alloys in the range 9–9½% aluminium. Fatigue tests at room temperature in air reveal no major difference between alloys with aluminium contents in the range 9–10½% aluminium. Some decrease in endurance limits was observed in tests at 400° C., and at this temperature the continued fall of the endurance limit with decreasing stress was more marked than at room temperature. Corrosion-fatigue tests showed that the aluminium bronzes were more resistant to corrosion-fatigue, in salt solution, than a stainless steel and stainless iron tested for comparison purposes.

I.—INTRODUCTION

THE use of complex aluminium bronzes for compressor blades in gas-turbine engines in recent years has stimulated studies of the mechanical properties, particularly the creep and fatigue properties, of these materials at moderately elevated temperatures. The work described here arose in this way, and in certain respects the programme carried out was influenced by this particular application of the alloys. Notably, attention was given to the selection of alloys which offer a good combination of forgeability at temperatures of the order of 900°–950° C. together with good resistance to creep and fatigue at temperatures of the order of 300°–400° C. However, the results obtained may well be of more general application, because alloys of this type appear to find rapidly widening fields of application.

II.—SCOPE OF THE WORK AND MATERIALS USED

Several series of materials were prepared and tested in this work. Certain differences in their preparation are described in detail below and are referred to subsequently in describing the test results.

Preliminary tests were carried out on specimens taken from forged bars with compositions within the range of Specification D.T.D. 197A, which covers aluminium contents from 8 to 11%, with iron and nickel from 4 to 6%, manganese up to 2.5%, balance copper. The creep properties of these specimens

proved to be very variable, possibly because of variations in the hot-working temperature, and all the subsequent work described in the present paper was carried out with hot-rolled bars or strips, which gave more consistent creep-test results.

In the first stage of the work, a series of eight alloys containing 5% each of nickel and iron, and with aluminium contents in the range 8.8–11.5%, was obtained from a commercial source in the form of 1-in.-dia. bars. These had been hot rolled, at an initial temperature of 900° or 950° C., from 4-in.-dia. billets and finished by two light (6%) cold-rolling passes with intermediate and final annealing treatments of 1 hr. at 700° C.

Three further alloys with the same iron and nickel contents and with aluminium contents in the range 9.7–10.7%, and containing in addition 0.3% manganese, were obtained from another industrial source as 1½-in.-dia. bars. These had been hot rolled from about 850° C. and were finished by machining with no cold reduction or annealing treatment.

Tests on these materials showed that it was desirable to examine alloys of lower aluminium content, and a further eight alloys were prepared with aluminium contents in the range 0–9.9%. These were rolled from 1-in.-thick castings to 16-gauge strip in the laboratory, following a rolling sequence similar to that used for the first series of eight alloys.

Though tests on the foregoing materials showed that alloys with aluminium contents below the lower limit of the D.T.D. 197A specification had better creep properties than alloys within the specification range,

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it was known that alloys of such low aluminium content were difficult to forge and that differences in forgeability were apparent within narrower ranges of aluminium content within the D.T.D. 197A specification range. The influence of aluminium content on the properties of the alloys was accordingly investigated in more detail by examining ten further alloys containing 5% each of nickel and iron, and with aluminium contents within the range 9.1–10.6%. These were hot rolled from 1-in.-thick castings to 0.1-in.-thick strip in the laboratory. Some of these were hot rolled from 950° C. and others from 900° C., and in all cases the strips were reheated to the nominal rolling temperature before each pass. Most of the materials were reduced to the final gauge with a 50% reduction in one pass; some were finished with lighter passes, 15 and 5%.

In the third stage of the work, an effort was made to improve the properties, especially the creep properties, of certain selected alloys by the addition of small amounts of high-melting-point elements, and, as in the second stage, the materials were hot rolled to 0.1-in.-thick strip at either 900° or 950° C. with intermediate reheating between passes, the last pass being 50% reduction in area. Alloys of two basic compositions were used, one containing 10.5% and the other 9% aluminium, both with 5% each of iron and nickel. Small amounts of high-melting-point elements were added to each basic alloy, the elements comprising chromium ($\frac{1}{2}$ and 1%), silicon, cobalt, and titanium (1 and 2% each). For convenience the alloys are referred to in the text as 9/5/5, 10.5/5/5, 9/5/5/1 Co, &c.

Additional materials used in this stage of the work and hot rolled in the same way were the alloys containing 7% aluminium with 5% each of iron and nickel (included since the earlier work had shown that the alloys with lower aluminium contents were the more creep-resistant) and alloys containing 7, 9, and 10.5% aluminium with 5% of iron only.

The materials prepared as outlined above were generally tested without further heat-treatment, apart from the 24 hr. at 300° or 400° C., which was necessarily given before starting creep and fatigue tests at these temperatures. In these cases materials are described as being in the as-received condition. In some cases the materials were heat-treated before test and details are given later.

In nearly all cases the iron and nickel contents of the alloys lay between the limits 4.8 and 5.2%. In a few instances they varied more widely from the nominal 5%, but the properties of these particular alloys did not appear significantly different on this account, and the details of iron and nickel contents are not recorded here. Four of the five lots of materials contained small amounts of manganese, while one was nominally manganese-free. No significant differences in properties could be attributed

to the presence or absence of manganese, and again the details of manganese contents are not included here. Analysis of appropriate samples revealed no segregation of major constituents in the materials, and the aluminium contents, the only major composition variable, are quoted in the tables and figures referred to later.

Spectrographic analysis for minor constituents showed that all the materials contained <0.007% lead, <0.01% tin, <0.001% bismuth, ~0.05% or less zinc, and the nominally silicon-free alloys contained ~0.03% or less of silicon.

III.—METALLOGRAPHY

The microstructures of many of these alloys are complex and difficult to resolve under the microscope. The examination and interpretation of the structures of the materials examined in this work was greatly facilitated by data provided by the Research Department of Imperial Chemical Industries, Ltd., Metals Division, through the courtesy of Dr. Cook. The information has since been published.¹ The broken lines of Fig. 1 are derived from these data; they define the phase fields in a section through the phase diagram for slowly cooled alloys containing 5% each of iron and nickel. The full lines in Fig. 1 are based on the present microscopic examination after reheating the hot-rolled materials to the various temperatures for short times and quenching. It appears that with short-time * heat-treatments such as might be imposed on the materials in practice, the structures are not very different from those defined by the work of Cook, Fentiman, and Davis.¹

The diagram is not dissimilar from the binary diagram for the copper–aluminium system.¹ However, in addition to the α , β , and δ phases present in the binary alloys, another phase, κ , is present, and the eutectoid occurs at a higher aluminium content. The κ phase is reported to have at room temperature an ordered body-centred cubic structure similar to that of NiAl and FeAl,¹ and is soluble in both the α and β phases, the solubility increasing with temperature until at temperatures of the order of 925°–950° C. it is completely dissolved. It appears as a blue-grey constituent sometimes with a brownish tinge, in the form of round particles, lamellæ, or rosettes, according to the mode of precipitation.

Alloys containing less than 3% aluminium were essentially α phase, but contained colonies of round particles of an unknown constituent, the colonies being elongated in the direction of rolling. They may have originated from coring in the cast materials. Apart from this feature, alloys to the left of the ($\alpha + \kappa$) field in Fig. 1 consisted of twinned equiaxial α grains.

In the as-received alloys containing about 4–7% aluminium, the κ phase was finely dispersed in the α matrix, generally appearing as small particles pre-

* The heat-treatments used were of the order of 1 hr. at temperatures from 700° to 950° C. and up to 24 hr. at lower temperatures.

precipitated on crystallographic planes. These alloys contained no β at the rolling temperature.

With higher aluminium contents (8–11% aluminium), the as-received alloys contained coarse and fine particles of κ phase distributed in both the α and the partially transformed β phases, the proportion of κ and of transformed β increasing with the aluminium content. The structure of the partially transformed β matrix was not resolved at magnifications exceeding 1000 diameters (see, for example, Fig. 12, Plate XIII).

The structures of alloys containing 9–11% aluminium varied considerably with their pretreatment. Alloys which had been hot rolled in the $(\alpha + \beta)$ or $(\alpha + \beta + \kappa)$ fields and then air-cooled had structures

As mentioned earlier, alloys quenched from the β , $(\alpha + \beta)$, or $(\alpha + \beta + \kappa)$ field have a matrix of partially transformed β with an acicular appearance, the detail of which structure is not fully resolved with the light microscope (see Fig. 15, Plate XIII). This matrix is very hard and alloys with this type of structure tend to be brittle. Fig. 2 shows the hardness of alloys quenched from various temperatures and includes a line AB above which are high hardness figures associated with brittleness. Reheating such materials at temperatures in the range 400°–700° C. completes the decomposition of the β phase and causes spheroidization of the κ (and δ) phases and results in softening.

Fig. 1 shows that the solubility of κ in α decreases rapidly as the temperature falls, and it has been found

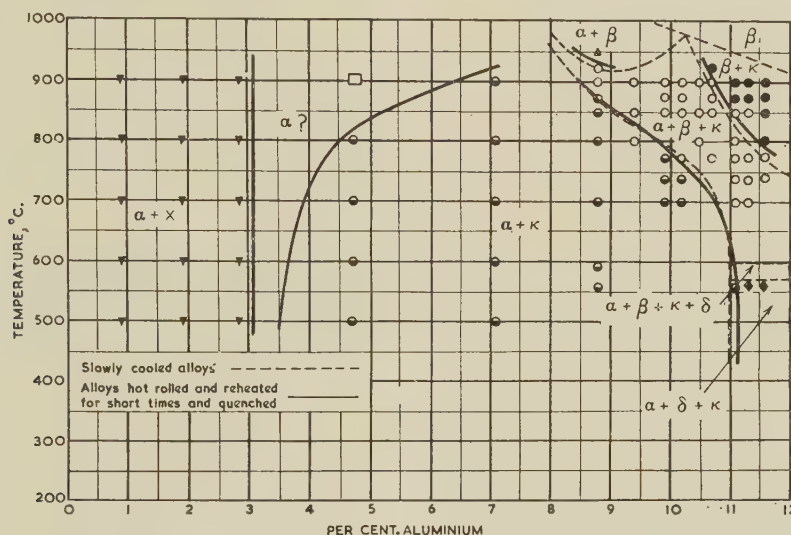


FIG. 1.—Section of Copper-Aluminium-Iron-Nickel Diagram at 5% Each of Iron and Nickel. Results for slowly cooled alloys from the work of Cook, Fentiman and Davis.¹

in which the α grains existing at the rolling temperature were clearly visible in a matrix of partly transformed β (Fig. 12). Heat-treatments of these materials at temperatures of the order of 600°–700° C. caused precipitation of κ in the α grains and spheroidization of the κ phase in the transformed β matrix (see, for example, Fig. 13, Plate XIII).

Alloys cooled fairly rapidly through the $(\alpha + \beta + \kappa)$ field frequently developed an acicular structure like that shown in Fig. 14 (Plate XIII). The structure is due to rapid separation of α from β , and on reheating at suitable temperatures in the $(\alpha + \beta + \kappa)$ field the α phase tends to form rounded crystals and the acicular structure is dispersed. In the present hot-rolled alloys with more than about 9% aluminium, the α phase appeared as stringers oriented in the rolling direction, the alloys having been rolled in the $(\alpha + \beta + \kappa)$ field, but structures like that in Fig. 14 were seen in some forged blades of alloys with aluminium contents of the order of 10–10.5%.

The feature of most importance from the point of view of the mechanical properties of the alloys is the breakdown of the β phase to $(\alpha + \kappa)$ or $(\alpha + \kappa + \delta)$.

that this may produce marked precipitation-hardening in alloys in which α predominates.

The structures of the alloys with 9 and 10.5% aluminium and 5% each of iron and nickel, and containing the additions of high-melting-point elements, were similar to those already described. Generally, the effect of the additional element was to slow down the breakdown of the β phase to the $(\alpha + \kappa)$ eutectoid.

A Note on the β -Phase Transformation in the Alloys

A small amount of work was carried out to determine the mode of breakdown of the β phase in aluminium bronzes containing 9–10.5% aluminium and 5% each of iron and nickel. Consideration of the equilibrium diagram (Fig. 1) indicates that the β phase which is present at high temperatures precipitates either one or two phases at lower temperatures. Metallographic examination has shown that the character of these phases depends on the rate of cooling from the single-phase β region, on the time and temperature of further low-temperature heat-treatments, and on the aluminium content.

Two alloys only were investigated, one containing

9.1% and the other 10.6% aluminium. These materials were heat-treated at temperatures at which they consist entirely of β , quenched, and then examined metallographically after various times of isothermal treatment at temperatures where two phases and three phases exist.

Pieces (approximately $\frac{3}{4} \times \frac{3}{8} \times \frac{3}{8}$ in.) of these alloys in the cast condition were treated for 1 hr. at

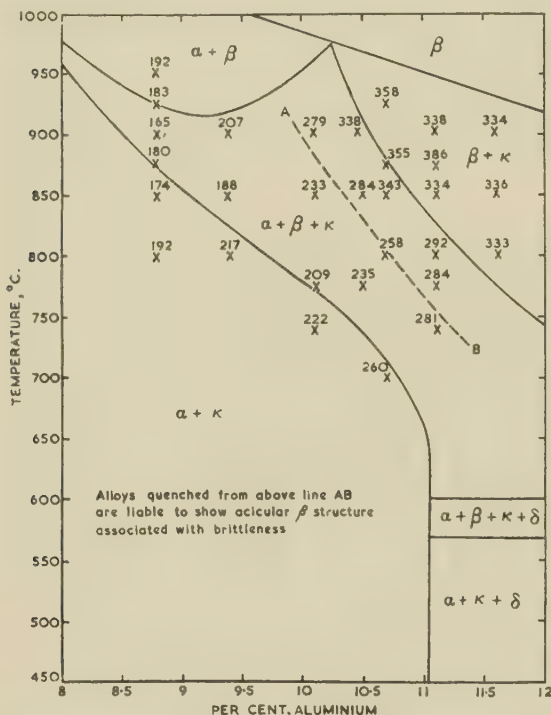


FIG. 2.—Results of Hardness Tests at Room Temperature on Quenched D.T.D. 197A Alloys Containing 5% Each of Iron and Nickel. Figures indicate diamond pyramid hardness numbers (20-kg. load).

1050° C. for the 9.1% aluminium alloy and 1000° C. for the 10.6% aluminium alloy. At these temperatures the alloys are in the β -phase field. After these treatments the specimens were quenched into brine at -10° C. to prevent, as far as possible, the β phase from breaking down. The 9.1% aluminium alloy was then reheated (a) at 950° C. and (b) at 900° C. for times of 20 sec., 1 min., 4 min., 10 min., and 40 min. The 10.6% aluminium alloy was reheated for the same times at 930° C. and at 850° C. All these heat-treatments were carried out in a salt bath, the specimens being quenched into water at 20° C. at the end of the heating times.

Examination of the materials quenched from the single-phase β field showed that they had an acicular structure similar to that illustrated in Fig. 15 (Plate XIII). It is suggested that this structure is formed by the incomplete transition of the body-centred cubic lattice of the β phase to a phase, hereafter called α' , having a distorted face-centred cubic lattice. A transformation similar to this occurs in the binary aluminium bronzes.²

In each alloy during isothermal treatment the mode of breakdown of the α' in the two-phase field was somewhat similar to that occurring in the three-phase field. For the sake of clarity, the characteristics of the precipitation (at temperatures corresponding to the three-phase fields) of the α and κ are described separately, although they actually occur simultaneously.

Photographs of the two alloys after 1, 10, and 40 minutes' treatment in their respective three-phase fields are shown in Figs. 16-21 (Plate XIV). The formation of α from the α' is different in the two alloys. In the 9.1% aluminium alloy α separates out mainly at grain boundaries, while the acicular structure within the grains becomes coarser and more Widmanstätten in appearance. In the 10.6% aluminium alloy α is first observed as thin films at the grain boundaries which do not grow during further treatment. Precipitation of α then takes place along crystallographic planes within the grains. At some time between 10 and 40 min. α ceases to precipitate along the crystallographic planes, but forms spheres which continue to grow in size with further time of treatment.

In both alloys κ appears at high magnifications, as finely dispersed particles within the grains with no apparent preference for the grain boundaries. As the time of heat-treatment is increased, further precipitation of κ occurs by the nucleation of more particles and not by the growth of existing particles.

IV.—MECHANICAL PROPERTIES

To specify the materials it was considered desirable to determine their mechanical properties, and it is emphasized that the results of the creep and fatigue tests quoted in this paper are probably characteristic only of materials prepared in the manner described, and having similar mechanical properties.

1. HARDNESS AND TENSILE PROPERTIES

In the as-received condition, the hardness of the alloys examined varied markedly. With aluminium contents from 2.8 to 8.8% the hardness values lay in the range 136-228 D.P.N., while for alloys of higher aluminium content the hardness ranged up to about 300 D.P.N., increasing with aluminium content.

The addition of small amounts of high-melting-point elements to the basis 9/5/5 and 10.5/5/5 alloys had little effect on their hardness in the as-received condition. The exception was the addition of 2% silicon, which markedly hardened and embrittled the 10.5/5/5 alloy.

When alloys with 9-10.5% aluminium were hot worked at 900° C. and air-cooled, the materials with the lower aluminium content hardened markedly on reheating at 400° C., while the alloys of relatively high aluminium content did not (see Fig. 3).

This hardening is attributed to precipitation of κ from solution in α . It is possible that hardening due

TABLE I.—Effect of Various Heat-Treatments on Room-Temperature Properties of an Alloy Containing 10.7% Aluminium with 5% Each of Iron and Nickel.

Heat-Treatment	Young's Modulus, lb./in. ² $\div 10^8$	Limit of Proportionality, tons/in. ²	0.1% Proof Stress, tons/in. ²	Tensile Stress, tons/in. ²	Elongation, % on 4V A	Hardness, D.P.N.	Type of Metallographic Structure
As-received	17.7	26.5	37.8	56.4	16	288	Rounded particles of coarse and fine κ in a matrix of α (Fig. 13, Plate XIII)
1 hr. at 925° C., A.C.	17.2	9.0	22.7	57.0	14	246	Coarse grained partially decomposed β with κ particles
1 hr. at 925° C., W.Q.*	14.8	4.5	26.7	59.8	3	375	Coarse grained acicular β with κ particles (Fig. 15, Plate XIII)
1 hr. at 925° C., W.Q. + 24 hr. at 400° C., A.C.†	17.9	14.5	45.3	63.8	8	365	Coarse grained acicular β + κ partially transformed to give extremely fine κ particles in matrix of α
1 hr. at 800° C., W.Q.	16.0	7.0	19.9	59.7	13	257	α + β + κ ; well defined islands of β
1 hr. at 800° C., W.Q. + 24 hr. at 400° C., A.C.	18.0	14.5	27.8	59.1	11	272	α + β + κ with the β islands partially or possibly completely transformed to α + κ

* Mean of 3 tests.

† Mean of 2 tests.

All other tests, single tests.

to this cause in the alloys of relatively high aluminium content, is obscured by softening due to spheroidization of the particles in the transformed β matrix.

Most of the hardening shown in Fig. 3 occurred in the first 24 hr. at 400° C., a treatment given to the hot-

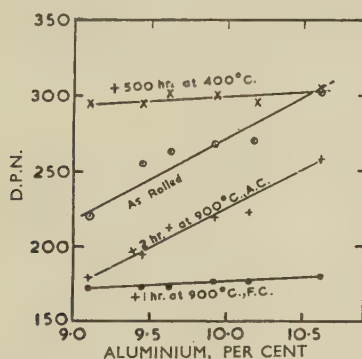


FIG. 3.—Hardness Values at Room Temperature. Effect of heat-treatment on materials rolled from 900° C. with 50% reduction and air-cooled.

rolled materials before loading in creep tests or cyclic stressing in fatigue tests at 400° C. Fig. 3 also shows the effect on the hardness of the alloys of two other heat-treatments on materials hot worked from 900° C. and air-cooled.

Ageing tests of 24 hr. duration on the 9/5/5 alloy at temperatures of 500°, 550°, and 600° C. showed the maximum hardness to be reached in 2–4 hr., the greatest increase being attained at 500° C. Heat-treatments of 2 hr. at 500° C. on the 9/5/5 alloys containing chromium and cobalt showed increases in hardness of about 25–30%.

The effects of heat-treatment at 300° and 400° C.

for periods up to 500 hr. on the alloys containing the high-melting-point elements were investigated. At 300° C. there was little or no effect on the hardness values, while at 400° C. most of the alloys increased in hardness slightly, the maximum hardness being attained in the first 24 hr.

Table I gives results of tensile tests on an alloy in the form of 1-in.-dia. rod and containing 10.7% aluminium after various heat-treatments. This material had been hot rolled from 900°–950° C., finished by two light (6%) cold-rolling passes with intermediate and final treatments at 700° C. The table includes a number of notes on the structures of the specimens, and the data illustrate the embrittling effect associated with the presence of the acicular partly transformed β in the structure of these alloys.

TABLE II.—Room-Temperature Tensile Properties of 0.1-in.-Thick Strip.

Hot rolled from 900° C.; 50% reduction. Results given are average of two tests.

Aluminium, %	0.1% Proof Stress, tons/in. ²	Tensile Strength, tons/in. ²	Elongation, % on 2 in.
9.11	33.3	52.0	12
9.46	36.6	56.9	9
9.63	37.0	59.0	10
10.14	41.0	63.2	6
10.62	38.3	58.9	1

Table II gives the tensile properties of the series of strips made by hot rolling without subsequent cold rolling and annealing. The alloys of relatively high aluminium content have little ductility because in the hot-rolled condition partially transformed β predominates in the structure.

In general, the additions of small amounts of high-melting-point elements to the basis 9/5/5 and 10.5/5/5

alloys slightly lowered the 0.1% proof stress, but had little effect on the tensile strength, elongation, and hardness.

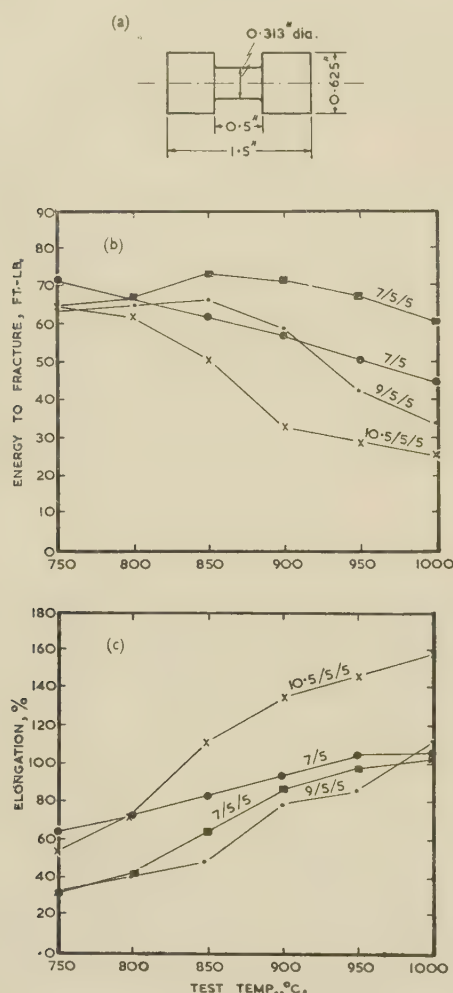


FIG. 4.—Elevated-Temperature Impact Tensile Tests. (a) The impact tensile specimen. (b) Energy to fracture. (c) Elongation on $\frac{1}{2}$ in. 7/5/5, &c., indicate percentages of Al/Fe/Ni.

Omitting the nickel from the three basis alloys reduced the 0.1% proof stress and hardness and increased the elongation, but did not affect the tensile strength.

2. HIGH-TEMPERATURE IMPACT TENSILE TESTS

To investigate the possibility of assessing the relative forgeability of the various alloys, high-temperature impact tensile tests were made on four selected alloys.

These tests were carried out in a 120-ft. lb. standard Izod impact-testing machine, using a modification described elsewhere,³ and the results obtained are shown in Fig. 4, together with the type of specimen used.

At 900°–950° C. (the normal forging temperature), the 10.5/5/5 alloy gave the lowest value of energy to fracture. This alloy is known to be easily forged, and using this as a basis of comparison, the other three

alloys would appear to be harder to forge, the 7/5/5 alloy being the least forgeable.

The energy values shown are those for energy to fracture, and the energy required in forging will be less than this. Hence, while it is not possible to assess accurately the energy required in forging, it is considered that the test has given a reasonable indication of the relative forgeability of the alloys. In particular, inspection of Fig. 4 suggests that if the 10.5/5/5 alloy forges satisfactorily at 850° C., a temperature of 900°–950° C. would be required for the 9/5/5 alloy, while the 7/5/5 type would be relatively stiff at these and considerably higher temperatures.

No indication of hot shortness between 750° and 1000° C. was shown by any of the alloys tested.

V.—CREEP PROPERTIES

The methods used to determine the creep properties have been described elsewhere⁴ and are not detailed in this report.

All the materials were tested in creep for 500 hr. at 400° C. at a stress of 4 tons/in.². In round specimens the diameter used was 0.357 in., while in strip specimens the thickness was 0.1 in. with a width of 0.5 in. The parallel length of both types of specimen was 5 in. Creep strains at the end of the 500-hr. period are taken as a criterion of creep-resistance in the discussion which follows. Some of the alloys were tested

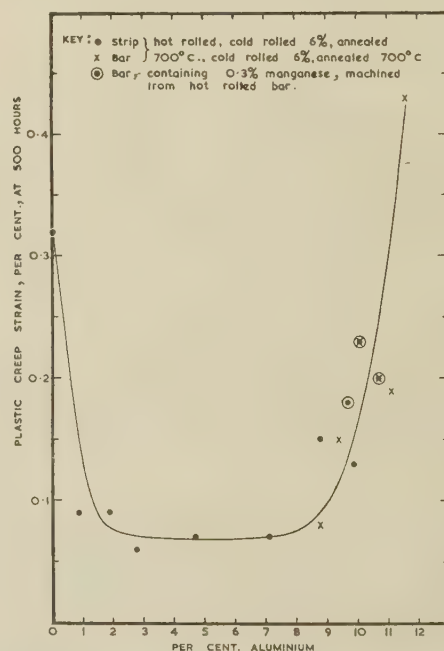


FIG. 5.—Effect of Aluminium Content on Creep at 400° C. and 4 Tons/in.² in Alloys Containing 5% Each of Iron and Nickel.

at several stresses at 300° and 400° C. for longer periods and the results are included in this paper.

All the alloys were tested in the as-received conditions described earlier, but it will have been noted that creep tests at 400° C. entail a 24-hr. soak at the

test temperature, and in some cases this caused marked precipitation-hardening in the alloys.

Fig. 5 shows creep strains after 500 hr. for alloys with aluminium contents up to 11.6%. Most of the

β phase at elevated temperatures and on this account are relatively stiff and difficult to forge. A main virtue of the complex aluminium bronzes for compressor blading lies in the good forging characteristics of some of the materials, and alloys containing 9–10.5% aluminium are of special interest for this reason; with aluminium contents above 10.5% the forged materials may have inadequate ductility. With these considerations in mind the effects of aluminium content and of hot-working treatment were examined in some detail for alloys with aluminium contents in the range named. Fig. 6 shows that their creep properties are significantly influenced by the hot-rolling procedure. When the final hot-rolling pass is light (5% reduction), the creep properties of alloys

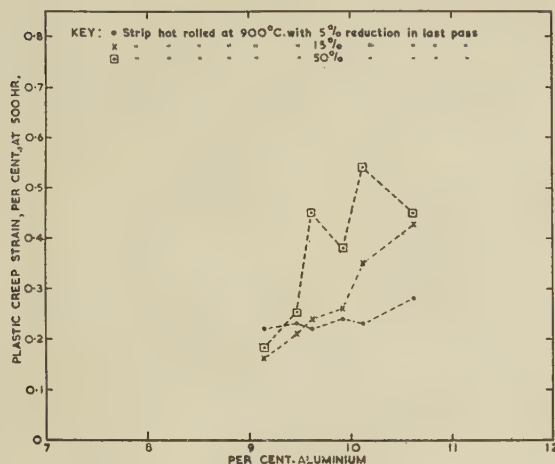


Fig. 6.—Effect of Final Hot-Rolling Pass on Creep at 400° C. and 4 Tons/in.².

materials were bars and strips made by hot rolling following by light cold rolling and intermediate and final annealing at 700° C., but three were not cold rolled and annealed in the later stages of fabrication. The creep properties of the latter are not notably different from those of the others, and it might be inferred that the light cold working and annealing has no marked effect on the creep properties of these alloys. However, as will be seen later, the creep properties are considerably affected by the hot-rolling procedure and variations in this may have obscured any effects due to the cold rolling and annealing. The main feature of interest in Fig. 5 is that the creep properties of the alloys of relatively low aluminium content, i.e. 1–7%, are significantly superior to those of the alloys with aluminium contents in the range covered by specification D.T.D. 197A. Alloys of very low aluminium content have poor resistance to oxidation, and it is likely that the

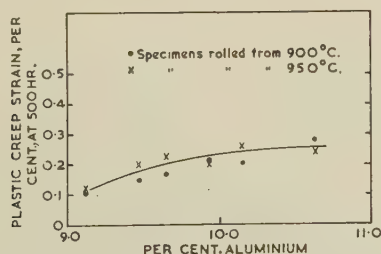


Fig. 7.—Creep Tests at 300° C. and 8 Tons/in.² on Hot-Rolled Strip Materials (Finished with 50% Reduction).

best combination of creep-resistance and resistance to scaling is given by alloys containing about 5–7% aluminium.

However, Fig. 1 shows that such alloys contain no

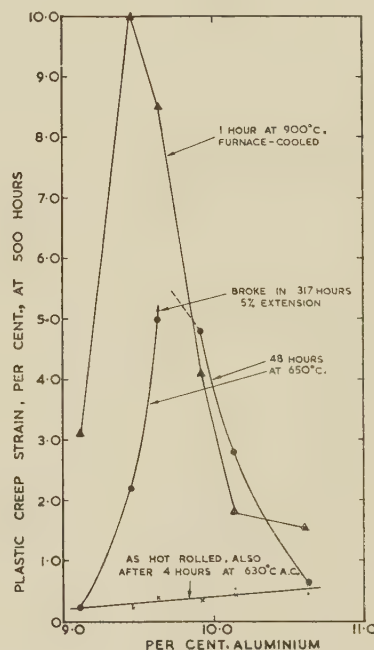


Fig. 8.—Effect of Heat-Treatment on Hot-Rolled (50% Reduction) Materials in Tests at 400° C. and 4 Tons/in.².

with 9–10.5% aluminium are very similar, and of the same order as those found in the other materials examined (cf. Fig. 5). With heavier hot reductions in the final pass, alloys with relatively high aluminium contents are less creep-resistant; in the range of alloys examined, only those with 9–9.5% aluminium are insensitive to the hot-rolling treatment.

The alloys containing 9–10.5% aluminium finished with a 50% hot reduction were also tested at 300° C. and 8 tons/in.²; the creep strains after 500 hr. are shown in Fig. 7, in which the slight superiority of the alloy with the lower aluminium content is again apparent.

Exploratory creep tests at 400° C. and 4 tons/in.² were also carried out on alloys with 9–11.6% aluminium after various heat-treatments, most of which involved quenching from temperatures in the range 800–900° C., with or without subsequent tempering

for 1 hr. at 600°–700° C. The results showed that the alloys containing up to about 9.5% aluminium were little affected by such heat-treatments; with higher aluminium contents the creep properties were either unchanged or were markedly impaired by the heat-treatments, the creep strains in 500 hr. in some cases

prolonged heat-treatment at 600°–700° C. caused a general coarsening of the microstructure, due to spheroidization of the κ phase, and this was associated with the reduction in resistance to creep.

The creep properties of α -phase aluminium bronzes are known to depend markedly on their grain-size

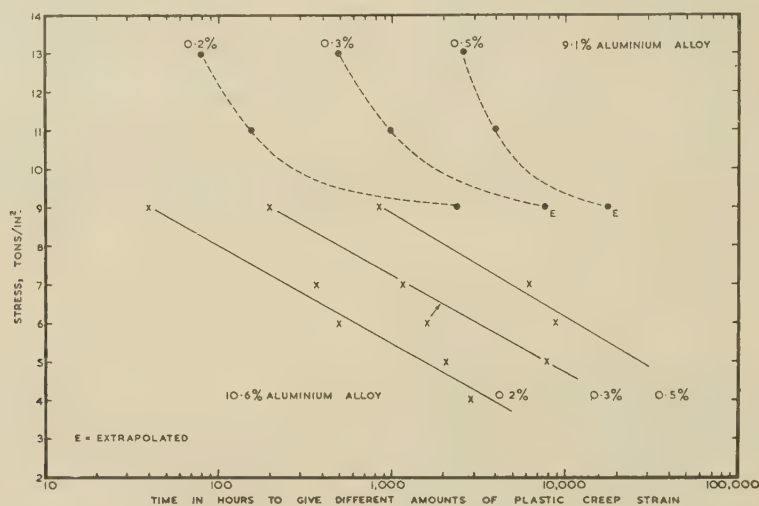


FIG. 9.—Long-Time Creep Tests at 300° C. on Hot-Rolled (50% Reduction) Materials.

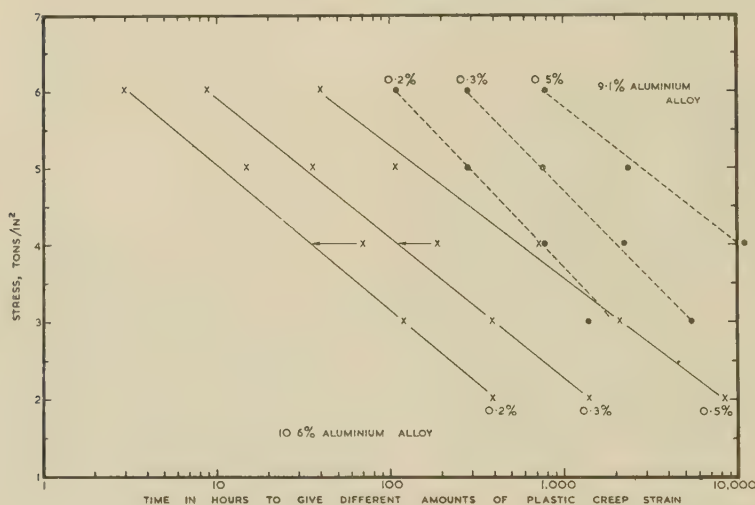


FIG. 10.—Long-Time Creep Tests at 400° C. on Hot-Rolled (50% Reduction) Materials.

(alloys with 9.7, 10.0, and 10.2% aluminium) increasing from about 0.25% for the as-received materials to 2 or 3% for the heat-treated alloys.

Heat-treatment of the as-received materials for a few hours at 600°–700° C. had no marked effect on their creep properties, but longer heat-treatments, e.g. 48 hr. at 650° C., caused considerable reduction in resistance to creep in some cases (see Fig. 8). Structural changes resulting from these heat-treatments could not be correlated with the changes in creep properties, except in the very general sense that

when tested at 500° C., and the same is probably true at 400° C. In the present work on the more complex alloys, efforts were made to estimate the size of the β crystals, from which α is formed at lower temperatures, to see whether this had any bearing on the creep properties, but no method was found to give a satisfactory estimate of this grain-size for materials in the as-received conditions.

Longer-time creep tests were carried out to provide data for design purposes in applications where long service lives are required. Two alloys in the as-rolled

conditions (final hot-rolling pass of 50%) and containing 9.1 and 10.6% aluminium were tested at 300° and 400° C. A range of stresses used at each temperature enabled diagrams to be prepared showing the relationship between stress and time to produce three different amounts of plastic creep strain. Each creep test was continued for 10,000 hr., and the results obtained are shown in Figs. 9 and 10.

The comparisons given in Table III are made on a basis of 2000 hours.

TABLE III.—Results of Creep Tests at 300° and 400° C.

Aluminium Content, %	At 300° C.			At 400° C.		
	Stress (tons/in. ²) for Plastic Creep Strain :			Stress (tons/in. ²) for Plastic Creep Strain :		
	0.2%	0.3%	0.5%	0.2%	0.3%	0.5%
9.1	9	10.1	...	2.7	4.0	5.2
10.6	5	6.3	7.9	0.4	1.7	2.6

These results confirm that the long-time creep strength of the alloy containing 9.1% aluminium is greater than that of the 10.6% aluminium alloy, and give confidence in the validity of the comparisons based on plastic creep strain at 500 hr. for all the materials.

Creep tests at 400° C. with a stress of 4 tons/in.² and at 300° C. with a stress of 8 tons/in.² were carried out on strip specimens of the 9/5/5 and 10.5/5/5 alloys containing the high-melting-point element additions.

The results of these tests showed that at both 400° and 300° C. the additional elements had little or no effect on the creep properties of the two basis alloys. This was also true when certain of the 9/5/5 class of alloys were heat-treated for 2 hr. at 500° C. before creep testing, the heat-treatment producing a 20–25% increase in hardness.

Omission of the nickel from the 10.5/5/5, 9/5/5, and 7/5/5 alloys markedly reduced their creep-resistance at both temperatures of testing. It is worthy of note that the 7/5/5 alloy gave the best creep properties of any of the alloys tested at both 400° and 300° C.

VI.—FATIGUE PROPERTIES

Rotating bending fatigue tests were carried out on materials hot rolled from 900° or 950° C. to a thickness of 0.25 in. and air-cooled, the final hot-rolling pass being a 50% reduction in thickness.

Tests were made at room temperature on specimens of the 9.1, 9.9, and 10.6% aluminium alloys and at 400° C. on the 9.0, 9.6, and 10.2% aluminium alloys.

Further tests on the 10.5/5/5, 9/5/5, 7/5/5, and 7/5 alloys were carried out in air at room temperature and also under corrosion conditions, the corroding medium being a 3% sodium chloride solution.

The B.N.F.M.R.A. rotating-load fatigue-testing machine⁴ was modified so that a flat-type specimen

(Fig. 11) could be tested. A description of the machine and the method of calibration, using round specimens, are given elsewhere.⁵ A similar method of calibration was used for the flat specimens, using calibration bars of the same geometrical shape as the specimens. To avoid resonance of these flat specimens, it was necessary to carry out the calibration and testing at a speed of 2400 r.p.m.

The surfaces of the specimens in the region of the maximum bending stress were polished with emery papers, the final polish being given by 0000 paper. All polishing was done in a longitudinal direction. The sharp corners, which might act as stress-raisers, were removed before polishing, the edges having a final radius of approximately $\frac{1}{16}$ in. White spirit was used as a lubricant during the polishing operations. When the specimen had been fitted with extension pieces, it was degreased with carbon tetrachloride before being inserted in the machine.

In the tests in the corrosive medium, the specimens were treated as above, and, when in the machine, the section at which the bending stress was a maximum was surrounded by two separated turns of fibre-glass tape. One end of the tape dipped into a beaker of

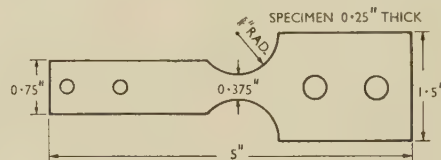


FIG. 11.—Flat-Type Specimen for Rotating Fatigue Tests.

3% NaCl solution held above the specimen, and the capillary action of the fibre-glass was sufficient to keep a film of the solution in contact with the specimen.

The results of the fatigue tests in air on the 7/5 and 7/5/5 alloys showed the alloy without nickel to withstand a slightly higher stress for a life of 25×10^6 cycles (± 16 tons/in.² against ± 14 tons/in.²), while the results of similar tests on the alloys containing 9.1, 9.9, and 10.6% aluminium and the 9/5/5 and 10.5/5/5 alloys indicated that these materials withstood a stress of ± 18 –20 tons/in.² for the same life. There was some indication of a fatigue limit in the latter alloys, i.e. a stress below which failure will never occur at this temperature.

The results at 400° C. for the alloys containing 9.0, 9.6, and 10.2% aluminium gave no indication of any one alloy being better than another, the materials withstanding a stress of about ± 17 tons/in.² for a life of 25×10^6 cycles. These tests, however, gave no indication of a possible fatigue limit, and it is suggested that this effect may be due to the slight, but continuing, oxidation of the surface of the specimen where the stresses are a maximum. In this sense, the fatigue tests at elevated temperature may be compared with corrosion-fatigue tests at room temperature.

Endurance limits considerably higher than those mentioned above have been quoted for alloys of this type hot worked in other ways. The relatively low

values found in this work are probably characteristic only of materials hot rolled to thin sections.

The results of the corrosion-fatigue tests on the 10.5/5/5, 9/5/5, 7/5/5, and 7/5 alloys showed the stress for a life of 25×10^6 cycles to be appreciably less than that withstood in air tests, the 10.5/5/5 and the 9/5/5 alloys withstanding about ± 11 tons/in.², while the other two alloys only withstood a stress of ± 9 tons/in.².

A summary of these results is given in Table IV.

TABLE IV.—*Fatigue Tests in Air and in Sodium Chloride Solution.*

Alloy	Stress (\pm tons/in. ²) for a Life of 25×10^6 Cycles	
	In Air	In 3% NaCl Solution
9 Al + 5 Fe + 5 Ni . . .	18.2	11.2
10.5 Al + 5 Fe + 5 Ni . .	19.8	11.0
7 Al + 5 Fe + 5 Ni . . .	13.7	9.4
7 Al + 5 Fe	16.2	8.8

To compare the fatigue and corrosion-fatigue properties of the 9/5/5 and 10.5/5/5 aluminium bronzes with those of other materials which may be of interest for the manufacture of gas-turbine compressor blades, some stainless steel materials were obtained from a commercial source. For convenience, in this paper, the alloy containing the lower chromium content and no nickel is referred to as "stainless iron".

These materials were in the form of rolled bar approximately $1\frac{3}{4} \times 1\frac{1}{2}$ in., which had been oil-quenched from 1000° C. in the case of the stainless iron and from 950° C. in the case of the stainless steel, and tempered at 700° and 650° C., respectively. These materials were tested without further heat-treatment, and the results of tensile tests are given in Table V.

TABLE V.—*Room-Temperature Tensile Properties of Stainless Iron and Steel.*

Alloy Composition	Tensile Strength, tons/in. ²	Elongation, % on 2 in.
13% Cr + 0.3% C	47.6	31
17% Cr + 1.5% Ni + 0.2% C	57.5	26

Fatigue tests were carried out on the stainless iron and steel specimens having the same geometrical shape as the complex aluminium bronze specimens, and the results of the tests are shown in Table VI.

Table VI shows that both the stainless iron and the stainless steel have superior fatigue-resistance to the complex aluminium bronzes in air at room temperature, the iron withstanding a stress of ± 24 tons/in.² and the steel a stress of ± 28 tons/in.², both for a life of 50×10^6 cycles, while the complex aluminium bronzes withstood a stress of only ± 18 to 19 tons/in.² for the same life.

However, under corrosion conditions in a 3% sodium chloride solution the positions were reversed, the complex bronzes withstanding a stress of ± 9 to

TABLE VI.—*Fatigue Tests in Air and in 3% Sodium Chloride Solution*

Alloy	Stress (\pm tons/in. ²) for a Life of 50×10^6 Cycles	
	In Air	In 3% NaCl Solution
Stainless Iron	24	4
Stainless Steel	28	7
9 Al + 5 Fe + 5 Ni	18	9
10.5 Al + 5 Fe + 5 Ni . . .	19	10

10 tons/in.², while the iron withstood a stress of only ± 4 tons/in.² and the steel only ± 7 tons/in.², all for the life of 50×10^6 cycles.

VII.—SUMMARY

The tensile, creep, fatigue, and corrosion-fatigue properties of some wrought complex aluminium bronzes, containing 0–11.5% aluminium and 5% each of iron and nickel, have been examined.

Room-temperature tensile tests have indicated that the mechanical properties of the alloys are dependent on the aluminium content and, at any given aluminium content, on the previous heat-treatment and resulting microstructure. Alloys with high aluminium contents and alloys heat-treated and quenched from the β , ($\alpha + \beta$), or ($\alpha + \beta + \kappa$) phase fields contain the acicular partially transformed β phase; where this type of structure was present, the alloys were brittle, with high tensile strengths and hardness and low elongations.

Elevated-temperature impact tensile tests showed that alloys in which the β phase predominated were more easily deformed, thus alloys with high aluminium contents would be more readily forged than alloys with low aluminium contents, in the range of composition considered here.

The creep properties of the alloys at 400° C. and a stress of 4 tons/in.² have been compared on the basis of plastic creep strain at the end of a 500-hr. testing period. Similar comparisons have been made at 300° C. and a stress of 8 tons/in.². The results showed that the creep-resistance of alloys containing between 1 and 7% aluminium was significantly superior to that of alloys with higher aluminium contents. Alloys containing less than 5% aluminium are known to have poor resistance to oxidation; hence the alloys which combine the best creep- and oxidation-resistance are those with between 5 and 7% aluminium. High-temperature heat-treatments and heat-treatments involving slow rates of cooling produced considerable structural changes in alloys of high aluminium content, and these changes were associated with a marked reduction in resistance to creep.

Separate additions of small amounts of chromium, silicon, cobalt, and titanium to alloys containing 9 and 10.5% aluminium and 5% each of iron and nickel, had little or no effect on the creep properties of the basis alloys. Hardening these alloys by heat-treatment at 500° C. before creep testing also had no effect on their creep-resistance.

Rotating bending fatigue tests in air at room temperature on alloys with aluminium contents of 9–10.6% showed these alloys to have an endurance limit of ± 18 –20 tons/in.² at 25×10^6 cycles, with some indication of a possible fatigue limit. Similar tests on a 7% aluminium alloy showed it to have an endurance limit of ± 14 tons/in.² for the same life. Higher endurance values have been reported for aluminium bronzes of this type, and the values given here evidently hold only for materials made as described.

At 400° C. the endurance limit at 25×10^6 cycles of the 9–10.6% aluminium alloys was ± 17 tons/in.², but with no indication of a fatigue limit at this temperature.

Under corrosion-fatigue conditions at room temperature, the endurance limit at 25×10^6 cycles of the

9 and 10.5% aluminium alloys fell to ± 11 tons/in.², while that of the 7% aluminium alloy fell to ± 9 tons/in.².

A comparison of these fatigue properties with those of a stainless iron and a stainless steel confirmed that in air the ferrous materials had the higher fatigue-resistance, but that in corrosion-fatigue tests the fatigue-resistance of the 9 and 10.5% aluminium bronzes was the higher.

ACKNOWLEDGEMENTS

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REFERENCES

1. M. Cook, W. P. Fentiman, and E. Davis, *J. Inst. Metals*, 1951–52, **80**, 419.
2. I. Obinata, *Mem. Ryojun Coll. Eng.*, 1929, **2**, (3), 205; 1930, **3**, (2), 87; 1931, **3**, (4), 285, 295.
3. B.N.F.M.R.A., unpublished work.
4. J. McKeown, *Metallurgia*, 1950, **42**, 189.
5. J. McKeown and L. H. Back, *ibid.*, 1948, **38**, 247.

1570 THE EFFECT OF STRAIN RATE AND TEMPERATURE ON THE RESISTANCE OF ALUMINIUM, COPPER, AND STEEL TO COMPRESSION *

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SYNOPSIS

Stress/strain curves were determined, during compression to 50% reduction of height at constant true strain rates in the range 1–40 sec.⁻¹, for (1) commercial-purity aluminium from –190° to 550° C., (2) phosphorus-deoxidized copper from 18° to 900° C., and (3) a 0.17% carbon steel from 930° to 1200° C. Glasses were used as lubricants at the higher temperatures. The stress/strain curves for copper at 750° and 900° C. and for steel showed a drop in stress at higher strains, unlike those for aluminium at 350°–550° C., which continued at approximately constant stress above a certain strain. The stress for a given strain increased with strain rate in fair agreement with a power law. The power index n tended to increase with temperature and at higher temperatures also increased with the strain. A plot of n against homologous temperature T_H (T_H = testing temperature (°K.)/m.p. (°K.)) gave a single curve for the three metals; n was small and almost constant for values of $T_H < \sim 0.55$, but increased approximately linearly with T_H above this value at a rate increasing with the strain.

I.—INTRODUCTION

RECENT advances in the theory of the rolling process, and the development of continuous rolling mills utilizing high speeds of deformation and heavy reductions, have shown the need for further investigation of the resistance of metals to deformation at strain rates and temperatures comparable with those used in industrial practice. Although it is well known that the resistance to plastic flow increases with increase in the strain rate and with decrease in temperature, there is little quantitative information available on the relation between these variables in compression. The present work was accordingly devoted to a study of the effect of these variables on the resistance to compression of aluminium, copper, and steel. A compression machine, “the cam plastometer” designed by Orowan and Los,¹ was used.

II.—APPARATUS AND MATERIALS

The experiments were carried out in a plastometer (Fig. 1, Plate XV) in which the specimen is compressed to 50% reduction in height at constant true strain rate between an upper platen attached to a load-measuring device and a lower platen driven by a rotating cam of logarithmic shape.² Various speeds can be obtained by a combination of motor field control and gear boxes. When constant speed is reached,

a trigger mechanism connects the lower platen with the cam, which compresses the specimen during one revolution.

An optical type of dynamometer is used which has the advantage of being free from inertia effects, simple, and comparatively insensitive to vibration. The load is measured by the birefringence created in two glass blocks. Plane polarized light, with the plane of polarization at 45° to the direction of compression, passes through these blocks, then through a Babinet Compensator and a polaroid which is crossed in relation to the polarizer. Load applied to the blocks causes the interference fringes produced by the Babinet Compensator to be displaced in a direction perpendicular to the fringes. This movement is recorded photographically on a drum mounted on the driving shaft. The dynamometer is calibrated periodically either after transferring to a compression machine or *in situ*, the specimen being replaced by a calibrated steel load cylinder^{3, 4} and loaded by means of the handwheel.

The instantaneous stress in the cylindrical specimen is calculated in the usual way, assuming homogeneous compression and correcting for the elastic distortion of the machine which amounted to 0.001 in./1000 lb. of load. The sensitivity may be judged from the fact that the maximum load of 10 tons caused a shift of ~ 16 fringe widths. The optical dynamometer is similar in some respects to one previously described.⁵

Three metals of commercial purity were used in the

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experiments: (1) as-extruded, $\frac{3}{4}$ -in.-dia. aluminium rod, (2) cold-drawn phosphorus-deoxidized, $\frac{3}{4}$ -in.-dia. copper rod, and (3) hot-rolled, 1-in.-dia. steel rod. The aluminium specimens were annealed for 1 hr. at 400° C. and the copper specimens for 2 hr. at 600° C. *in vacuo* before testing. The steel specimens needed for "static" tests were annealed for 2 hr. at 890° C. *in vacuo*; the others were not annealed. The suppliers' analyses (wt.-%) were as follows:

Aluminium:	Cu	Si	Mn	Fe	Mg	Zn	
Batch (a)	0.10	0.20	0.02	0.46	...	0.01	
Batch (b)	0.01	0.20	0.01	0.46	0.01	0.01	
	P	Ni	Sn	Sb	Pb	Fe	Mn
Copper	0.018	0.0010	0.0003	0.0002	0.0005	0.0010	0.0020
	Mn	As	Bi	S	O	Se, Te	
	<0.0005	<0.0005	<0.0001	0.0014	>0.003	not detected	
	C	Mn	Si	S	P		
Steel	0.17	0.62	0.153	0.054	0.032		

The stress/strain characteristics of the materials were determined by conventional (static) tests in a Denison compression machine, loading in increments and with one exception relubricating the specimen after each increment (Fig. 2). The exception was an aluminium specimen which was first relubricated after 4 tons had been applied, corresponding to point X in Fig. 2 and was thereafter treated in the same way.

The specimens were cylinders 25.00 ± 0.02 mm. in height, and either 12.00 or 18.00 ± 0.02 mm. in dia. according to the material and the temperature of testing. The specimen axis was parallel to the extrusion or the rolling direction. Specimens were

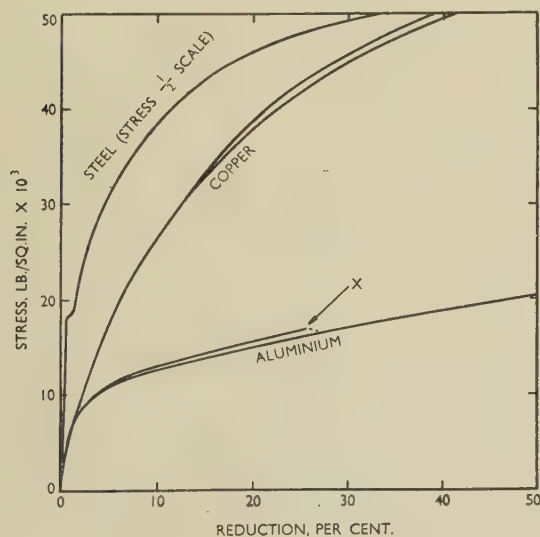


FIG. 2.—"Static" Stress/Strain Curves Determined on a Denison Compression Machine.

heated or cooled to the desired temperature and then quickly transferred to the plastometer and compressed. Temperature change during transfer was minimized by enclosing the specimen in a hollow-walled guard-

ring box made of Nimonic 80 alloy (Fig. 3). Sintered titanium carbide platens were used, and the specimen was centred in the box by means of a foil annulus. The temperature change before compression began did

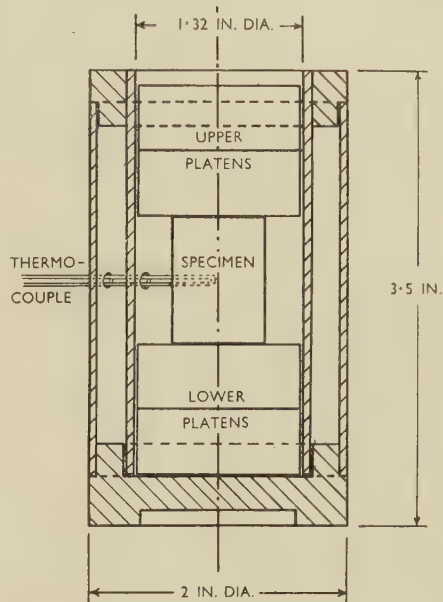


FIG. 3.—Final Pattern of the Guard-Ring Box, with the Specimen in Position. The thermocouple is removed before compression.

not exceed 2° C. at temperatures below 900° C., and probably did not exceed 5° C. at 1200° C. Specimens were heated in resistance-type furnaces, using an argon atmosphere in the case of the steel specimens. Refrigeration of the guard-ring box plus specimen was

TABLE I.—Compositions of Glasses Used as Lubricants and Their Useful Temperature Ranges.

Glass . . .	A	B	C	D (Pyrex)	E
Temp. Range, °C.	450–600	600–750	850–1000	1000–1100	1100–1200
SiO ₂ , %	...	27.3	69	80	55
B ₂ O ₃ , %	20	...	1.2	12	7
BaO, %	3
Al ₂ O ₃ , %	3.4	3	21
CaO, %	6.1	...	14
MgO, %	3.2
PbO, %	80	71
Na ₂ O, %	16.2	4	...
K ₂ O, %	...	1.5	0.7	0.3	...

achieved by immersion in a vacuum flask containing liquid nitrogen (–190° C.) or pentane cooled by adding either liquid nitrogen (–120° C.) or excess solid carbon dioxide (–75° C.).

The end faces of the specimens were lubricated with petroleum jelly at room temperature, graphite

("Aquadag") at temperatures up to about 450° C., and powdered glasses (Table I) at temperatures above 450° C. It was found that the glasses which proved to be satisfactory lubricants had a viscosity of $\sim 10^4$ poises at the temperature of operation.

The copper specimens were completely coated with glass powder, which was applied as a suspension in

results. The difference between the stress values obtained on duplicate specimens for 20 and 40% reduction in height was computed for 42 pairs of aluminium specimens, 30 pairs of copper specimens, and 22 pairs of steel specimens. The arithmetic mean deviation in stress values was less than 100, 170, and 380 lb./in.² for aluminium, copper, and steel,

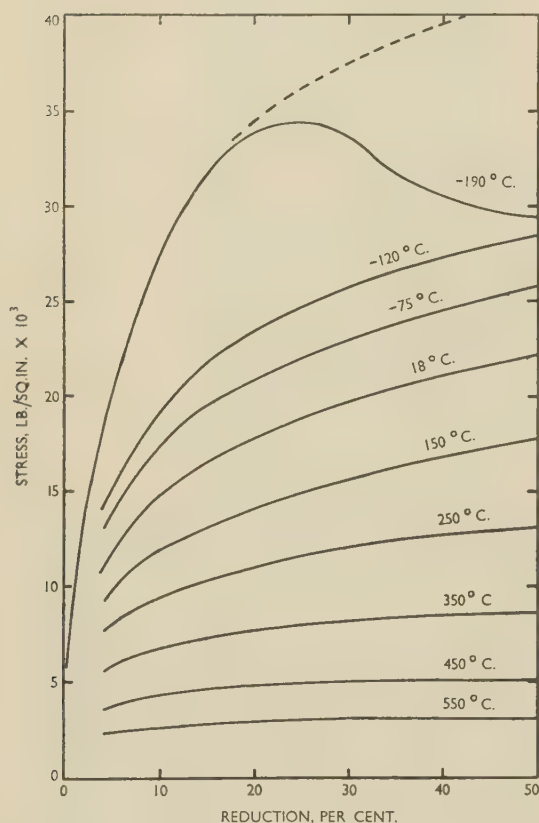


FIG. 4.—Effect of Temperature on the Stress/Strain Curve for Aluminium. Strain rate = 4.38 sec.⁻¹
(Average stresses plotted.).

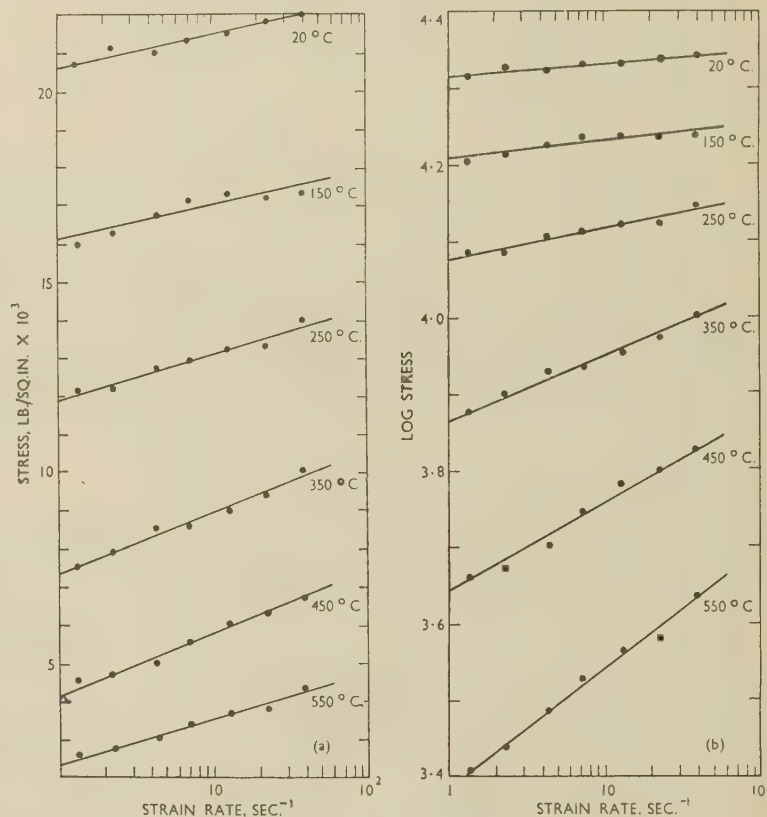


FIG. 5.—Effect of Strain Rate on the Stress Required to Compress Aluminium to 40% Reduction at Various Temperatures.
(a) σ v. $\log_{10} \dot{\epsilon}$; (b) $\log_{10} \sigma$ v. $\log_{10} \dot{\epsilon}$.

alcohol or ether. When a specimen was placed in the hot furnace, the glass coating rapidly formed a viscous film which to a large extent prevented further oxidation of the specimen.

III.—EXPERIMENTAL RESULTS

Experiments were made to determine the effect of temperature on the stress required to compress aluminium, copper, and steel to 50% reduction in height at various strain rates in the range 1–40 sec.⁻¹ (Tables II–IV). The temperature range explored was –190° to 550° C. for aluminium, 18°–900° C. for copper, and 930°–1200° C. for steel. The stress values are in most cases the average of two or more

respectively. Some values taken from "static" curves (Fig. 2) are included in Tables II–IV.

Fig. 4 shows typical stress/strain curves at various temperatures for aluminium strained at 4.38 sec.⁻¹. Increase in temperature lowered the stress required to effect a given homogeneous compression. Fig. 5 illustrates the effect of strain rate on the stress required to compress aluminium 40% at various temperatures. Increase in strain rate tended to increase the stress required to effect a given compression. The results for copper and steel give similar curves.

It will be noted that two sizes of specimens were used in these experiments, according to the material and the temperature. The effect of specimen diameter on the stress/strain relationship is shown by

results obtained on aluminium at 18° C. and 4.38 and 12.9 sec.⁻¹ (Table II), on copper at 600° C. and 4.35, 12.9, and 39.3 sec.⁻¹ (Table III), and steel at 1000° C.

TABLE II.—*Effect of Temperature and Strain Rate on Stress Required to Compress Aluminium.*

Batch	Specimen Dia., mm.	Temp., °C.	Strain Rate, sec. ⁻¹	Average Stress (10 ³ lb./in. ²) to Compress :				
				10%	20%	30%	40%	50%
b	12	—190	4.38	28.1	34.1	33.9	32.2	31.6
b	12	—120	4.38	18.6	22.4	24.7	26.3	27.8
b	12	—75	4.38	17.4	20.9	23.0	24.5	25.8
a	18	—75	4.38	16.0	19.5	21.5	23.0	24.1
a	18	18	slow*	12.9	15.4	17.0	18.8	20.5
a	18		1.34	14.7	17.2	19.0	20.7	22.1
a	18		2.31	14.9	17.6	19.5	21.1	22.6
a	18		4.38	14.1	17.0	19.2	21.0	22.4
b	12		4.38	14.5	17.2	19.2	20.6	21.9
a	18		7.15	14.6	17.5	19.5	21.3	22.9
a	18		12.9	15.1	17.9	19.8	21.5	23.0
b	12		12.9	15.0	17.9	19.7	21.1	22.3
a	18		23.1	15.3	18.2	20.1	21.8	23.1
a	18		39.3	15.1	18.1	20.1	22.0	23.3
a	18	150	1.34	11.4	13.5	14.9	16.0	16.9
			2.31	11.5	13.8	15.3	16.3	17.2
			4.38	11.9	14.1	15.6	16.7	17.8
			7.15	12.0	14.2	15.7	17.1	17.9
			12.9	12.0	14.2	15.9	17.3	18.2
			23.1	12.1	14.2	15.8	17.2	18.4
			39.3	12.1	14.3	16.0	17.4	18.5
a	18	250	1.34	9.2	10.6	11.5	12.1	12.5
			2.31	9.4	10.7	11.6	12.2	12.6
			4.38	9.5	11.0	12.1	12.7	13.1
			7.15	9.6	11.1	12.1	12.9	13.1
			12.9	9.8	11.6	12.6	13.3	13.6
			23.1	9.8	11.5	12.6	13.4	13.8
a	18	350	1.34	6.3	7.0	7.3	7.5	7.5
			2.31	6.3	7.1	7.6	7.8	7.9
			4.38	6.8	7.7	8.2	8.5	8.6
			7.15†	6.7	7.6	8.2	8.6	8.7
			12.9	7.0	8.1	8.6	9.0	9.1
			23.1	7.3	8.3	9.0	9.4	9.7
			39.3	7.7	8.8	9.5	10.0	10.2
a	18	450	1.34	4.0	4.5	4.6	4.6	4.5
			2.31	4.2	4.6	4.8	4.7	4.7
			4.38	4.4	4.9	5.0	5.0	5.1
			7.15	4.8	5.3	5.5	5.6	5.6
			12.9	5.4	5.8	5.9	6.0	6.1
			23.1	5.2	5.9	6.2	6.3	6.4
			39.3	5.8	6.2	6.5	6.7	6.9
a	18	550	1.34	2.3	2.5	2.6	2.6	2.6
			2.31	2.5	2.8	2.8	2.8	2.7
			4.38	2.7	2.9	3.1	3.1	3.1
			7.15	3.0	3.3	3.3	3.4	3.4
			12.9	3.1	3.4	3.6	3.7	3.7
			23.1	3.2	3.6	3.8	3.8	3.8
			39.3	3.7	4.0	4.2	4.3	4.4

* Static test in Denison compression machine.

† Specimen barrelled.

and 4.35 and 7.4 sec.⁻¹ (Table IV). In most cases, specimens of 12 mm. dia. required a slightly higher stress to produce ~10% compression and a slightly lower stress to produce ~50% compression than specimens of 18 mm. dia.

If deformation is homogeneous, then a cylindrical

specimen should retain its shape during compression. The lubricants employed were effective in preventing barreling to a very large extent. When barreling occurred, the results were discarded and the test repeated. Tests on aluminium at room temperature showed that the use of a lubricant (petroleum jelly) decreased the average load required to carry out a given compression by about 2½%. On the 12-mm.-dia. specimens, where the height:diameter ratio was

TABLE III.—*Effect of Temperature and Strain Rate on Stress Required to Compress Copper.*

Specimen Dia., mm.	Temp., °C.	Strain Rate, sec. ⁻¹	Average Stress (10 ³ lb./in. ²) to Compress :				
			10%	20%	30%	40%	50%
12	18	slow *	26.6	38.4	45.4	50.0	53.4
		4.35	27.3	40.9	49.2	54.4	56.0
		7.4	26.6	40.3	49.2	54.5	57.3
		12.9	27.1	40.3	49.0	54.9	57.4
		23.1	25.1	39.4	48.9	54.5	57.1
12	150	4.35	23.6	32.6	38.0	41.7	44.5
		7.4	23.8	33.5	39.4	43.6	46.6
		12.9	23.9	33.7	39.9	44.0	47.2
		23.1	24.2	34.4	40.0	44.5	46.9
12	300	4.35	20.8	27.5	31.5	34.8	36.8
		7.4	21.0	27.6	31.1	33.4	35.3
		12.9	20.6	27.4	31.2	34.2	36.8
		23.1	21.4	28.2	32.2	35.0	37.3
		39.3	21.4	28.2	32.1	35.0	37.5
12	450	4.35	17.5	22.8	25.9	27.7	29.0
		7.4	17.7	22.9	25.5	27.0	28.1
		12.9	17.5	22.7	25.7	27.7	29.1
		23.1	17.2	22.4	25.4	27.5	29.2
		39.3	17.3	22.9	25.9	28.2	30.1
18	600	1.34	13.1	17.0	19.2	19.7	17.0
18		4.35	13.8	18.1	20.5	21.8	21.4
12		4.35	14.4	18.1	20.1	21.0	21.1
18		12.9	14.1	18.8	21.3	23.2	23.7
12		12.9	14.8	18.5	20.3	21.5	22.3
18		39.3	15.0	19.9	22.7	24.6	25.4
12		39.3	15.7	19.5	21.9	23.5	24.5
18	750	1.34	7.8	10.1	9.6	8.8	8.7
		4.35	8.9	11.1	12.3	11.1	10.8
		12.9	9.7	12.6	14.1	14.4	13.1
		39.3	10.8	13.8	15.6	16.6	16.8
18	900	1.34	5.5	6.9	6.5	6.0	5.7
		4.35	5.7	7.3	7.7	7.0	6.7
		12.9	6.6	8.5	9.4	9.2	8.3
		39.3	7.7	9.6	10.8	11.2	11.0

* Static test in Denison compression machine.

~2, a shearing effect was encountered, the specimens tending to shear over during the test and to become S-shaped in the extreme case. The degree of instability increased as the testing temperature was lowered. Some copper specimens showed this effect at room temperature. All the aluminium specimens tested at —190° C. were unstable, so that the curve for homogeneous compression above ~20% strain was not determined (Fig. 4). When the effect was severe, the stress did not increase steadily with the percentage reduction as observed when homogeneous compression occurred, but dropped off at reductions above ~20%.

With the exception of the aluminium tests at -190°C. , the results of all tests in which marked shearing occurred were discarded.

TABLE IV.—Effect of Temperature and Strain Rate on Stress Required to Compress Steel.

Specimen Dia., mm.	Temp., $^{\circ}\text{C.}$	Strain Rate, sec. ⁻¹	Average Stress (10^3 lb./in. ²) to Compress:				
			10%	20%	30%	40%	50%
18	18	slow *	77.5	92.0	98.0	102	105
12	930	4.35	18.6	22.3	23.5	23.9	24.1
		7.4	19.0	22.9	25.1	26.4	26.2
		12.9	20.9	24.0	25.8	27.0	27.1
		23.1	21.6	25.3	27.4	28.6	29.4
12	1000	4.35	14.8	18.3	20.0	20.7	20.1
		4.35	14.8	17.9	19.6	20.8	20.3
		7.4	16.4	19.2	21.0	22.1	22.0
		7.4	15.5	18.6	20.8	22.3	22.2
		12.9	16.9	19.7	21.4	22.6	22.8
		23.1	18.6	21.6	22.9	23.9	24.4
18	1060	4.35	12.8	15.2	16.6	17.1	16.3
		7.4	13.6	16.0	17.9	18.7	18.5
		12.9	14.5	16.9	18.6	19.9	20.2
		23.1	15.4	18.4	20.3	21.7	22.1
18	1135	4.35	11.0	12.9	13.8	13.8	13.1
		7.4	11.6	13.6	14.8	15.3	14.7
		12.9	12.4	14.5	15.8	16.7	16.9
		23.1	13.6	15.9	17.4	18.3	18.5
18	1200	4.35	9.0	10.6	11.0	10.9	10.1
		7.4	9.5	10.9	11.7	11.8	11.2
		12.9	10.2	11.6	12.5	12.7	12.5
		23.1	10.9	12.6	13.7	14.3	14.0

* Static test in Denison compression machine.

IV.—DISCUSSION

1. STRESS/STRAIN CURVES

Where shearing effects were absent, the stress/strain curves obtained for aluminium were smooth and showed no unusual features. Although softening must have been occurring during compression at temperatures in the range 350° – 550°C. , no drop in stress was observed at higher strain as in the case of copper and steel. After a certain strain had been reached, deformation continued at approximately constant stress (Fig. 4), only a slight "ripple" showing on the record.

The curves for copper were smooth at low temperatures, but became wavy at 600°C. and above, presumably owing to softening effects becoming appreciable during compression. At 750° and 900°C. an actual drop in stress occurred during compression at reductions over $\sim 40\%$, indicating that softening (recrystallization) was predominating over strain-hardening.

The curves for steel at 930° – 1200°C. showed similar features to copper, tending to be wavy, particularly at the higher temperatures, and often showing a fall in stress above $\sim 40\%$ reduction.

Previous workers have attempted to derive a single

equation expressing the stress in terms of strain, strain rate, and temperature. Lubahn⁶ obtained such an equation containing six constants from three empirical relationships. He assumed the true stress/strain curve to be a simple power law for large strains. This assumption was supported by tensile-test data obtained on a number of materials by Fusfeld⁷ and by Low and Garofalo,⁸ but was in poor agreement with the results of Dorn, *et al.*^{9, 10} The stress/strain curves obtained in the present work could not be expressed by a power law, with the exception of curves obtained on aluminium at room temperature, where the value of the index was about $\frac{1}{2}$. Other possible equations have been reviewed by, for example, Hollomon¹¹ and Osgood,¹² but in view of the change in shape of the stress/strain curve observed in the present work on copper when the temperature was raised, it seems unlikely that any single function can be found to express the relation between stress and strain for all three metals over the range of variables.

2. EFFECT OF STRAIN RATE ON THE RESISTANCE TO COMPRESSION

Since the time available for softening varies with the strain rate and the rate of softening will vary with the strain, no simple relationship can be expected between the stress and the strain rate in the temperature range where softening occurs during a test.

The stress/strain curve for copper at 750°C. at a strain rate of 12.9 sec.^{-1} showed a drop in stress above $\sim 40\%$ reduction, indicating that softening and strain-hardening were nearly in balance in the region of 40% reduction, so that the stress should be particularly sensitive to a change in strain rate. This was observed to be the case.

The stress required for a given compression tended to increase with the strain rate at all temperatures (Table II–IV). Aluminium, however, showed a marked strain-rate effect at room temperature, whereas copper showed only a small effect.

The effect of strain rate on the stress for a given strain could be expressed to reasonable approximation either by the semi-logarithmic formula of Ludwik¹³:

$$\sigma = A \ln \dot{\epsilon} + \sigma_0 \quad (1)$$

or by the power law:

$$\sigma = \sigma_0 \dot{\epsilon}^n \quad (2)$$

where σ is the stress for a given strain, σ_0 is the stress at unit strain rate for that strain, $\dot{\epsilon}$ is the true strain rate, and A and n are constants.

Thus the graphs of σ against $\log_{10} \dot{\epsilon}$ and of $\log_{10} \sigma$ against $\log_{10} \dot{\epsilon}$ were both approximately linear, but the power law appeared to provide a slightly better interpretation of the data. Fig. 5, for 40% reduction, is typical of the results obtained for the three metals. Deviations from linearity were most marked in the tests on steel and in those on copper at 750° and 900°C.

Sokolov^{14–18} similarly concluded from compression

tests on lead, tin, zinc, aluminium, copper, nickel, brass, and several steels, over a range of strain rates from 10^{-3} to 10^2 sec.^{-1} and at temperatures from 20°C. to their respective melting points, that the power law provided a better interpretation of the effect of strain rate. On the other hand, a number of American workers¹⁹⁻²³ found from compression tests at 10^2 – 10^3 sec.^{-1} on copper at room temperature that the stress was proportional to the logarithm of the strain rate for a given strain (up to 25% compression). Many workers have investigated the effect of strain rate on the tensile properties, among whom may be mentioned Ginns,²⁴ Elam,²⁵ Jones and Moore,²⁶ and Manjoine and Nadai.²⁷ The last-named, working on aluminium,

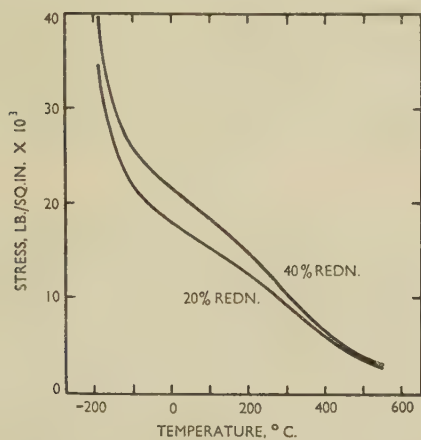


FIG. 6.—Effect of Temperature on the Stress Required to Compress Aluminium to 20% and 40% Reduction. Strain rate = 4.38 sec.^{-1} .

copper, and steel at strain rates of 10^2 – 10^3 sec.^{-1} and elevated temperatures, found that the ultimate true stress varied approximately linearly with the logarithm of the strain rate, in agreement with the results of Jones and Moore²⁶ on the yield and tensile strength of fourteen metals tested at room temperature at strain rates up to $10^{-1} \text{ sec.}^{-1}$.

MacGregor and Fisher²⁸ suggested combining the effect of strain rate and temperature, so that a series of tensile tests with only one variable instead of two would determine the behaviour. A "velocity-modified temperature", T_m , was defined such that:

$$T_m = T(1 - k \ln \dot{\epsilon}/\dot{\epsilon}_0) \quad (3)$$

where T = absolute testing temperature, k = a constant, $\dot{\epsilon}$ = true strain rate of the test, and $\dot{\epsilon}_0$ = unit strain rate, which was taken as $10^{-3} \text{ sec.}^{-1}$.

This relation gives the expected qualitative result that an increase in strain rate is equivalent to a decrease in temperature. The detailed results obtained here, however, do not support this conception, except as an approximation at temperatures below that at which softening effects become important. The effect of temperature on the stress for the compression of aluminium increases sharply below a temperature of about -100°C. (Fig. 6), so that, although

no measurements were made of the effect of strain rate, it seems unlikely that equation (3) will hold at very low temperatures.

3. EFFECT OF TEMPERATURE

The stress for a given compression and strain rate varied with temperature in a complex manner, as illustrated by the results obtained on aluminium (Fig. 6). The curve for copper is similar in shape.

The slope of the $\log_{10} \sigma$ against $\log_{10} \dot{\epsilon}$ plots tended to increase progressively with temperature, whereas the slope of the σ against $\log_{10} \dot{\epsilon}$ plots varied with temperature, but in no consistent manner over the whole range of temperature (Fig. 5). Equation (2) is therefore more suitable than equation (1) for interpolation at intermediate temperatures. Values of n are given in Table V, and it will be seen that they are similar in magnitude for the three metals.

Values of n showed little variation with strain for aluminium at 18° and 150°C. , but increased with strain in the range 250° – 550°C. Similarly in the case of copper and steel, the biggest numerical change in n occurred at the higher testing temperatures, where softening would be expected to occur appreciably during compression.

TABLE V.—Values of the Index n in the Equation $\sigma = \sigma_0 \dot{\epsilon}^n$.

Metal	Temp., °C.	Value of n for a Compression of :				
		10%	20%	30%	40%	50%
Al	18	0.013	0.018	0.018	0.018	0.020
	150	0.022	0.022	0.021	0.024	0.026
	250	0.026	0.031	0.035	0.041	0.041
	350	0.055	0.061	0.073	0.084	0.088
	450	0.100	0.098	0.100	0.116	0.130
	550	0.130	0.130	0.141	0.156	0.155
Cu	18	0.010	0.001	0.002	0.006	0.010
	150	0.014	0.016	0.020	0.023	0.026
	300	0.016	0.018	0.017	0.025	0.024
	450	0.010	0.004	0.008	0.014	0.031
	600	0.050	0.043	0.041	0.056	0.078
	750	0.096	0.097	0.128	0.186	0.182
	900	0.134	0.110	0.154	0.195	0.190
Fe	930	0.088	0.084	0.094	0.099	0.105
	1000	0.108	0.100	0.090	0.093	0.122
	1060	0.112	0.107	0.117	0.127	0.150
	1135	0.123	0.129	0.138	0.159	0.198
	1200	0.116	0.122	0.141	0.173	0.196

The variation of n with temperature for the three metals can be represented in one graph by plotting n against the homologous temperature, T_H , where

$$T_H = \frac{\text{testing temperature } (^\circ \text{K.})}{\text{melting-point temperature } (^\circ \text{K.})}$$

as in Fig. 7 for 40% reduction. Irrespective of the metal and strain, n remains small and shows little change with T_H at values of T_H below ~ 0.55 , but increases approximately linearly with T_H above ~ 0.55 , the rate of increase being greater the higher the percentage reduction. Sokolov¹⁷ concluded from

tests on four steels over a range of strain rates from 10^{-3} to 10^2 sec. $^{-1}$ (50% compression) that n was proportional to T_H , but contrary to the present work he found that the extrapolated curve passed through the origin.

The values of n given above in Table V, when plotted against T_H , can, for purposes of interpolation,

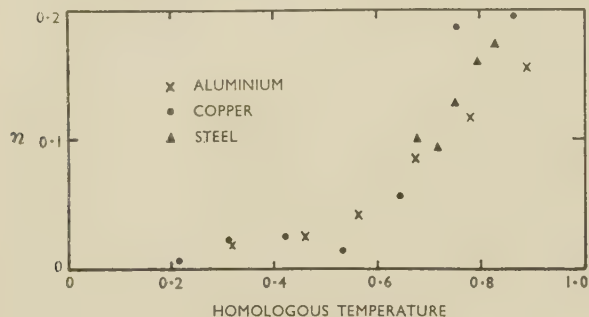


FIG. 7.—Dependence of the Strain-Rate Effect on the Homologous Temperature for 40% Reduction.

be represented by two straight lines, the first passing through the origin and continuing to the ordinate $T_H = 0.55$ and the second beginning at the point so reached. The slopes of the two lines for various compressions are given in Table VI.

TABLE VI.—Values of the Slopes of the n/T_H Curve for Various Compressions.

Compression, %	10	20	30	40	50
m_1^*	0.045	0.050	0.055	0.060	0.065
m_2^\dagger	0.36	0.38	0.41	0.46	0.52

* m_1 is the slope for $0 < T_H < 0.55$.

† m_2 is the slope for $T_H > 0.55$.

TABLE VII.—Values of σ_0 in the Equation $\sigma = \sigma_0 \dot{\epsilon}^n$.

Metal	Temp., °C.	Value of σ_0 for a Compression of:				
		10%	20%	30%	40%	50%
Al	18	14.6	17.1	18.9	20.6	22.0
	150	11.4	13.5	15.0	16.1	17.0
	250	9.1	10.5	11.4	11.9	12.3
	350	6.3	6.9	7.2	7.3	7.4
	450	3.9	4.3	4.5	4.4	4.3
	550	2.2	2.4	2.5	2.4	2.4
Cu	18	26.3	40.3	49.0	54.1	55.7
	150	23.1	32.4	37.8	41.5	43.5
	300	20.2	26.5	30.2	32.2	34.4
	450	17.0	22.5	25.1	26.6	26.8
	600	12.7	16.8	18.9	19.4	19.0
	750	7.6	9.7	10.0	8.5	8.2
	900	4.7	6.3	6.1	5.5	5.2
Fe	930	16.3	19.4	20.4	20.9	20.9
	1000	13.0	15.6	17.3	18.0	16.9
	1060	10.9	12.9	14.0	14.4	13.6
	1135	9.1	10.5	11.2	11.0	9.9
	1200	7.6	8.6	8.8	8.3	7.6

The values of σ_0 , the stress at unit strain rate, obtained from the graphs of $\log_{10} \sigma$ against $\log_{10} \dot{\epsilon}$, are shown in Table VII.

From these tables and the equation $\sigma = \sigma_0 \dot{\epsilon}^n$, the stress for any intermediate percentage reduction at any temperature can be estimated by interpolation and calculation.

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REFERENCES

1. E. Orowan, *B.I.S.R.A. Restricted Rep.*, 1950, (MW/F/22/50).
2. N. Loizou and R. B. Sims, *J. Mechanics Physics Solids*, 1953, **1**, 234.
3. Brit. Patent No. 626,206, 1949.
4. J. Rankine, W. H. Bailey, and F. P. Stanton, *J. Iron Steel Inst.*, 1948, **160**, 381.
5. E. Orowan, F. H. Scott, and C. L. Smith, *J. Sci. Instruments*, 1950, **27**, 118.
6. J. D. Lubahn, *J. Appl. Mechanics*, 1947, **14**, 229.
7. H. I. Fushfeld, *J. Appl. Physics*, 1949, **20**, 1052.
8. J. R. Low, Jr., and F. Garofalo, *Proc. Soc. Exper. Stress Analysis*, 1947, **4**, (2), 16.
9. J. E. Dorn, P. Pietrowsky, and T. E. Tietz, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, **188**, 933.
10. O. D. Sherby, R. A. Anderson, and J. E. Dorn, *ibid.*, 1951, **191**, 643.
11. J. H. Hollomon, "The Problem of Fracture". 1946: New York (American Welding Society).
12. W. R. Osgood, *J. Aeronaut. Sci.*, 1946, **13**, 45.
13. P. Ludwik, "Elemente der technologischen Mechanik". 1909: Berlin (Springer).
14. L. D. Sokolov, *Zhur. Tekhn. Fiziki*, 1946, **16**, 437.
15. L. D. Sokolov, *ibid.*, 1947, **17**, 543.
16. L. D. Sokolov, *ibid.*, 1948, **18**, 93.
17. L. D. Sokolov, *Doklady Akad. Nauk S.S.S.R.*, 1949, **67**, 459.
18. L. D. Sokolov, *ibid.*, 1950, **70**, 839.
19. F. Seitz, A. W. Lawson, and P. Miller, *O.S.R.D. Rep.*, 1942, (495) (NDRC A41).
20. F. Seitz, A. W. Lawson, and P. Miller, *ibid.*, 1942, (619) (NDRC A63).
21. F. Seitz, *ibid.*, 1943, (1388) (NDRC A174).
22. O. C. Simpson, E. L. Fireman, and J. S. Koehler, *ibid.*, 1944, (3330) (NDRC A257).
23. G. H. Winslow and W. H. Bessey, *ibid.*, 1945, (5039) (NDRC A324).
24. D. W. Ginn, *J. Inst. Metals*, 1937, **61**, 61.
25. C. F. Elam, *Proc. Roy. Soc.*, 1938, [A], **165**, 568.
26. P. G. Jones and H. F. Moore, *Proc. Amer. Soc. Test. Mat.*, 1940, **40**, 610.
27. M. Manjoine and A. Nadai, *ibid.*, 1940, **40**, 822.
28. A. Nadai and M. Manjoine, *J. Appl. Mechanics*, 1941, **8**, 77.
29. C. W. MacGregor and J. C. Fisher, *J. Appl. Mechanics*, 1946, **13**, 11.

THE SELECTIVE OXIDATION OF NICKEL-CHROMIUM 1571 ALLOYS AT HIGH TEMPERATURES *

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SYNOPSIS

The mechanism of selective oxidation of a nickel-4.6% chromium alloy has been studied between 800° and 1250° C., using mixtures of hydrogen and water vapour as oxidizing agent.

The morphology of the oxide formed on the surface of the alloy differs markedly from the surface structure of the unoxidized metal. Nucleation of Cr_2O_3 is followed by its coalescence; at a later stage the primary oxide evaporates and the bare metal takes on a striated appearance.

Various aspects of the observations are discussed, in particular the surface striations. In an oxidizing atmosphere, the surface of the specimen may be considered not as a free-metal/atmosphere boundary, but as a metal/oxide interface. Selective oxidation of the chromium contributes to the building-up of this surface oxide film; when the temperature is sufficiently high, the lattice of the metal beneath undergoes a reorganization, as a result of which the metal surface is enabled to adopt the micro-profile corresponding to its state of minimum free energy.

I.—INTRODUCTION

WHEN a nickel-rich nickel-chromium alloy is exposed to the air under atmospheric pressure at a temperature above 1000° C., the surface becomes covered with a compact layer of oxide of uniform thickness composed of two phases: nickel monoxide, NiO , and nickel chromite, NiCr_2O_4 . In a recent paper,¹ the mechanism of formation of these phases and the isothermal development of the system at various temperatures between 1000° and 1300° C. were examined.

When the oxidizing power of the atmosphere is progressively reduced, the reactions described are replaced by a process of selective oxidation, the more readily oxidized element—in this case the chromium—alone becoming oxidized at the surface of the alloy.

The conditions most favourable for observing the selective oxidation depend upon the equilibrium set up between the alloy and the gaseous phase under consideration. The present investigation was confined exclusively to water-vapour/hydrogen mixtures, it being easy to vary the oxidizing power of such mixtures over a wide range.

The conditions used were as follows: temperature range 800°–1250° C.; water-vapour/hydrogen pressure ratio 6.5×10^{-3} to 5.9×10^{-2} . It has been found that under these conditions oxidation of chromium always takes place to the exclusion of the oxidation of nickel, such atmospheres being reducing with respect to pure nickel and alloys in which nickel largely predominates.

II.—PREPARATION AND TREATMENT OF SPECIMENS

The material used for the experiments was a nickel-4.6% chromium alloy, specially prepared by melting

the pure metals in an induction furnace under an argon atmosphere. The results of analysis were as follows: $\text{Al} < 0.005$, $\text{C} = 0.010$, $\text{Si} < 0.010\%$, Mn and Mg not detected.

Preliminary work had shown that reproducibility of the experiments was largely dependent upon the surface condition of the alloy. An attempt was therefore first of all made to establish a method of surface preparation which would reduce to a minimum defects of microgeometric or physicochemical origin and at the same time be easy to repeat.

The specimens were in the form of small plates 0.3–0.5 mm. thick and several square centimetres in area. After being mechanically polished with abrasives of increasing fineness, they were washed with alcohol and benzene and then electrolytically polished in a phosphate-glycerine bath (H_3PO_4 ($d = 1.71$) 300 c.c., glycerine ($d = 1.26$) 530 c.c., H_2O 90 c.c., 100°–110° C., 12 V.). Treatment for 10 min. resulted in a surface which appeared flawless under the microscope. The specimens were finally heated for several hours at 1200° C., in an atmosphere of pure dry hydrogen. The best method of checking the surface finish was found to be that making use of interference colours, which is recommended by Bardolle² in his study of pure iron. The specimens are subjected for several minutes to atmospheric oxidation at about 500° C. If the surface so obtained is satisfactory, the colours are clear and uniform over the whole of each crystal. The slightest physical or chemical imperfections give rise to local variations in colour and, if they are sufficiently numerous, may even obliterate the distinction between one crystal and another. The same method affords a means of following changes in crystal structure of the metal during selective oxidation.

The procedure used for the selective oxidation of

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the alloys in water-vapour/hydrogen mixtures was as follows:

Commercial hydrogen was completely freed from all remaining traces of oxygen by being passed over platinized asbestos held at a suitable temperature in an electric-resistance furnace. The water formed was absorbed first by bubbling through concentrated sulphuric acid, and then by passing over activated alumina and phosphoric anhydride dispersed in pumice.

The saturator consisted of a chamber containing water, the temperature of which was thermostatically controlled to $\pm 0.2^\circ\text{C}$. The hydrogen took up water vapour in passing through a sintered glass diffuser. The composition of the water-vapour/hydrogen mixture was regulated by suitably adjusting the temperature of the water in the saturator. A mullite tube, of the Norton type (1000 mm. long and 26–35 mm. in dia.), which is practically impermeable to gas even at high temperatures, formed the reaction chamber. The gas mixture from the saturator entered the tube at one end. The metal specimens were introduced into the reaction zone from the other end of the tube by means of an electromagnetic device operated from outside. The specimens could thus be rapidly introduced into the reaction zone or withdrawn from it while perfect gas-tightness was maintained. The central part of the tube was heated by a silicon carbide resistor furnace, automatically controlled to $\pm 5^\circ\text{C}$, the temperature being measured by means of a platinum/platinum-rhodium thermocouple.

III.—EXPERIMENTAL RESULTS

Using the apparatus described above, a wide range of tests was carried out by varying the reaction temperature and the partial pressure of the water vapour in the atmosphere. Isothermal conditions were always maintained; the duration of the tests depended on the speed of the reaction and varied from a few minutes to several hours, according to the temperature. After treatment the specimens were examined microscopically and by electron diffraction. It was found that the structure of the oxide formed on the alloy and the surface structure of the unoxidized areas of metal differed considerably, depending on the conditions of test. However, they always bore some relationship to one another, and it was often possible to observe the gradual transition from one to the other, when the temperature, the partial pressure of water vapour, or these two factors simultaneously, were continuously varied. It is thus possible to summarize all the experimental observations in the form of a graph, taking as abscissa the treatment temperatures and as ordinate the partial pressures of the water vapour in the oxidizing mixture. Tests leading to similar types of reaction fall into definite regions of such a diagram (Fig. 1).

REGION I: PRIMARY NUCLEATION

This region corresponds to the lowest temperatures and partial water-vapour pressures that can give rise to an appreciable reaction. For example, a specimen oxidized at 900°C . in an atmosphere having a $\text{H}_2\text{O}:\text{H}_2$ pressure ratio of 6.5×10^{-3} becomes covered with innumerable oxide particles distributed uniformly over each crystal. The average dimensions of the particles are very small—much less than 1μ . Their number, though always large, varies from one crystal to another, so that at low magnifications the

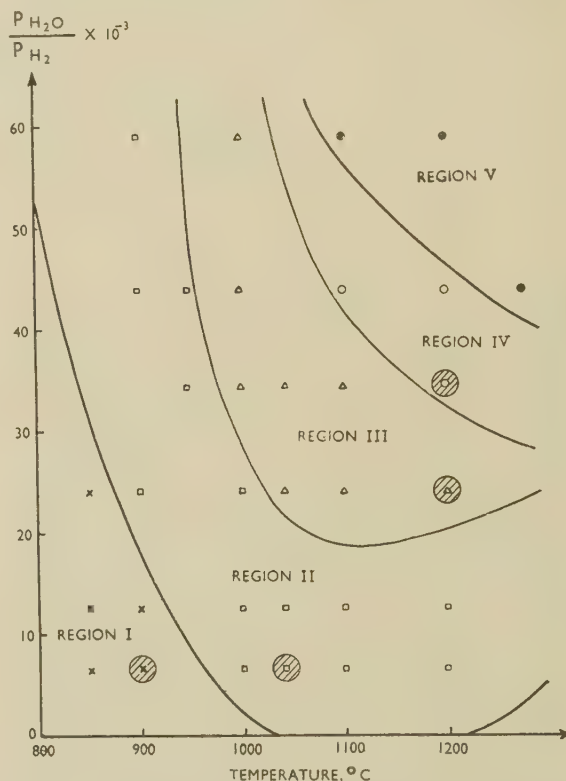


Fig. 1.—Summary of Experimental Conditions Adopted for the Various Tests, Showing the Different Regions. Points corresponding to conditions typical of the various regions are surrounded by large circles.

various crystals appear to be covered with an oxide layer of unequal density which distinguishes them sharply from one another (Figs. 2 and 3, Plate XVI). Under these conditions the selective oxidation thus takes place in a discontinuous manner on the surface of the metal, and the degree of oxidation depends on the orientation of the crystals.

Moreover, there is frequently visible at the boundary of neighbouring crystals a narrow band in which the metal is free from oxide. In general, the disposition of these bands is unsymmetrical in relation to the grain boundaries, the wider part always occurring in the crystal on which the oxide particles are less numerous. Furthermore, the greater the difference in density of the surface oxide layers on the two

sides of the boundary, the more marked are the bands.

This type of oxidation reveals extremely clearly the structure of the alloy by the sharp distinction it brings out between the grain boundaries and the twinning planes.

REGION II: NUCLEATION AND RECRYSTALLIZATION

This region corresponds to temperatures and partial pressures of water vapour slightly higher than those in Region I. For instance, if selective oxidation is carried out at 1040° C. in an atmosphere with $H_2O : H_2$ pressure ratio of 6.5×10^{-3} , the formation of oxide particles takes place as before, but their average dimensions are much greater. On the other hand, they are generally less abundant than in Region I (Fig. 4, Plate XVI). There is still a relationship between their number and the orientation of the underlying crystal surface, but the oxide-free bands at the inter- and intra-crystalline boundaries are much less marked than in Region I.

It may be supposed that in this region the oxide particles pass very rapidly through an intermediate, highly dispersed state similar to that of Region I, but that the rise in temperature or in partial pressure of water vapour stimulates the onset of recrystallization, thus leading to an increase in size and reduction in number of the particles.

REGION III: COALESCENCE OF THE OXIDE

When still higher temperatures and partial pressures of water vapour are employed, a distinct change takes place in the appearance of the oxide. At the same time characteristic alterations appear in the metal surface.

As regards the oxide, formation of particles takes place fairly rapidly at first, and these tend to coalesce when the selective-oxidation treatment is continued. This coalescence may be considered as a further development of the tendency already observed in Region II, but it proceeds much more actively and

By extrapolation to very short times, values are obtained which vary greatly in accordance with the orientation of the metal, thus demonstrating the influence on nucleation of the structure of the underlying metal, already apparent in Regions I and II. During coalescence the oxide particles arrange themselves in parallel lines, the orientation of which is governed by the crystal lattice of the metal; in particular, the lines undergo sharp changes of direction on crossing twinning planes (Fig. 5, Plate XVI).

Parallel with this development of oxide, the metal surface undergoes a progressive transformation which was not observed at any time in Region II. It loses its initial smoothness and there appear between the areas covered with oxide, surface relief effects, the form of which is dependent upon the crystal structure of the metal. Sometimes these take the form of parallel ridges, at other times of scales overlapping in a very regular manner. On crossing a grain boundary or a twinning plane, their orientation changes sharply in accordance with the general change in orientation. It is difficult to estimate exactly the differences in level involved, but they are certainly less than 1μ .

REGION IV: EVAPORATION OF THE OXIDE AND STRIATION OF THE METAL

The nature of selective oxidation at temperatures and under pressures very much higher than those of Region III will now be considered, taking as an example a temperature of 1200° C. and a $H_2O : H_2$ pressure ratio of between 3.20 and 4.20×10^{-2} . After treatment under these conditions, the appearance of the specimens is highly characteristic. In the first place there is a very marked increase in the formation of the surface relief effects which made their first appearance in Region III. Within a few hours the whole metal surface is covered with striations, the outlines of which are extremely sharp (Figs. 6, 7, and 8, Plates XVI and XVII). Each crystal exhibits in general only one set of parallel striations. Very occasionally a second set appears having a different orientation, thus running contrary to the general regularity of the phenomenon (Fig. 9, Plate XVII). In the neighbourhood of the grain boundaries the striations undergo changes of orientation and take on the shape of the intercrystalline grooves which appear simultaneously during the course of the treatment. Within a particular metal crystal, progressive changes of orientation and sometimes sharp deviations appear in certain cases. Figs. 10-13 (Plate XVII), which are electron micrographs taken at a magnification of 2500, illustrate these points.

When a specimen exhibiting these phenomena is treated either in highly purified hydrogen or argon, the striations disappear and the surface once more takes on a specular finish (Fig. 14, Plate XVIII). At 1200° C. this result is obtained after a few minutes in

TABLE I.—*Number of Particles of Oxide Found on a Ni-Cr Crystal Surface after Oxidizing Treatment for Various Periods.*

Treatment Time, min.	10	30	60	90	120	150	180	300
Specimen Ref.	Number of Particles of Oxide							
N381 .	136	108	96	...	80	...	72	...
N384 .	188	160	140	...	128	...	116	...
N385 .	256	224	204	...	180	...	172	...
N3709 .	376	312	276	248	...	232	...	168

can be followed as a function of time by counting the grains. Table I shows the change with time of the number of grains of oxide on a given area of surface, counted on different metal crystals.

hydrogen and after a longer period in argon. This suggests an explanation of the mechanism of formation of the striations, which will be considered in further detail in Section IV.

The formation of surface relief effects on the metal is accompanied by the development of islands of compact oxide of considerable dimensions, distributed in a sporadic manner over the surface of the specimen. Their position and their structure prove that they bear no relation to the crystal lattice of the underlying metal; in particular, their outlines are oriented quite haphazardly in relation to the striations (Fig. 15, Plate XVIII). Interference colours reveal that these islands are of only slight thickness.

To be able to relate this new development to the phenomena observed at lower temperatures and partial pressures of water vapour, it was thought desirable to make a detailed study of the oxidation of the specimens at constant temperature. After a very brief period the metal becomes covered with a thin greyish layer of oxide which on examination at higher magnifications proves to be made up of very small grains of oxide in juxtaposition. At this stage the reaction is similar to that observed in Region I. But the surface appearance rapidly changes. The layer of oxide particles tends to be reabsorbed in certain places and at the same time the striated zones make their appearance. The latter seem to form preferentially at points where oxide particles initially existed. This development does not take place with equal speed at all points on the surface; in certain favourable cases it is possible to observe the different stages coexisting on the same specimen (Fig. 16, Plate XVIII).

A careful study of these developments suggests a mechanism by which the initially uniform oxide disappears through the medium of the gaseous phase. Part of the oxide thus eliminated is redeposited at certain points on the specimen, contributing to the growth of the islands of crystallized oxide. Another part of the oxide is deposited on the walls of the reaction tube, where it can easily be identified. It may be noted that it is only at relatively high partial pressures of water vapour that the oxide is removed in the gaseous phase.

A characteristic feature of the earlier observations had been that the orientation of the system of parallel striations was obviously closely related to the crystal structure of the metal beneath. It was thought interesting to determine whether this orientation corresponded to traces of any particular planes of the lattice. A study of eighty crystals, in some ten specimens, gave the following results. The orientation of the striations of chemical origin could readily be compared with those produced in the same crystals by mechanical stress, e.g. by bending. Bending causes the appearance of three systems of slip lines which in the majority of cases consist of traces of (111) planes on the free surface. By reference to these orientations, it was found that the system of striations revealed by selective oxidation always

corresponds to a (111) direction, which consequently is superimposed on one of the family of slip lines produced by deformation. This result has been further confirmed by the study of etch figures on a number of crystals. It is interesting to note that in general the oxidation process leads to the appearance of only one system of striations and that from among the various pairs of (111) planes which might occur, it is always that pair which includes the plane forming the smallest angle with the free surface of the metal that appears. It is the solution which, in reducing the free surface to elements of (111) planes, reduces the number of surface asperities to a minimum. The above reasoning can be strictly applied only when the free surface of the specimen lies in zone with the intersection of pairs of (111) planes, and when this condition is not satisfied—as it is not in the majority of cases—it is necessary to assume that faults occur here and there and a fresh system of (111) planes appears. This may lead in some cases to the appearance of a secondary system of striations (Fig. 17).

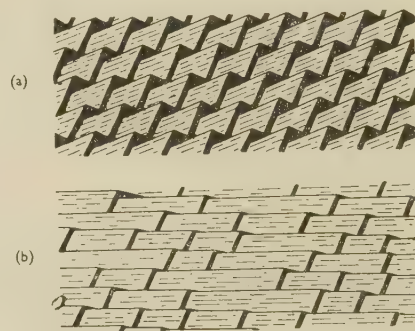


FIG. 17.—Schematic Representation of the Surface Relief Effects Observed in (a) Region III and (b) Region IV.

REGION V: CONTINUOUS OXIDE LAYER

At partial pressures of water vapour corresponding to a $\text{H}_2\text{O} : \text{H}_2$ ratio of the order of $5 \cdot 10 \times 10^{-2}$ and at temperatures above 1100°C ., there develops on the surface of the metal a compact layer of chromium sesquioxide, Cr_2O_3 , the thickness of which increases as a function of time. Coalescence is no longer found in this region, the reaction probably being too rapid for it to appear.

As may be appreciated from the foregoing description, a study of the selective oxidation of nickel-chromium alloys under varying conditions of temperature and of water-vapour pressure reveals some very diverse features. These features are not completely irreconcilable with one another. In particular, there is reason to believe that in the experiments described the morphological characteristics noted in Regions III and IV are always preceded by those belonging to Regions I and II, although for reasons of kinetics it is not always possible to observe the intermediate stages.

It will be noticed that at temperatures above 1100°C . (Fig. 1, p. 88) the boundaries of Regions

I-II and II-III are displaced towards higher water-vapour pressures. As a result, it is necessary at these temperatures to increase the pressure of water vapour in order to be able to observe the same phases as at lower temperatures. This apparent anomaly is due to the proximity at such temperatures of the region where there is a reversible reduction of Cr_2O_3 by water-vapour/hydrogen mixtures.

IV.—DISCUSSION

In the experimental work described certain observations seem to allow some general conclusions to be drawn, and it is proposed to discuss these in further detail, particular attention being devoted to the following points: nature of the process of primary nucleation, specific phenomena occurring at the boundaries of the crystalline regions, formation and disappearance of surface relief effects on the metal.

It was found that under conditions of moderate reactivity oxidation takes place at particular places on the surface of the alloy, and there is every reason to believe that under conditions of higher reactivity the initial mechanism of the reaction preserves, at least temporarily, this discontinuous character. This fact may be regarded as an extension of observations made recently by Bardolle and Bénard³ on the controlled oxidation of iron at high temperatures. Under oxygen pressures of the order of 10^{-3} mm. Hg, iron becomes covered with particles of oxide, the number and orientation of which are related to the crystal orientation of the metal. The differentiation is, however, less sharp in the case of the selective oxidation of nickel-chromium alloys than in that of pure iron. There is nothing surprising in this, for in the case of the pure metal the formation of the oxide at certain definite spots on the surface is, if local impurities are excluded, dependent entirely upon the crystal structure, while in the case of the alloy it can be visualized that the development of a particle of Cr_2O_3 at one point involves the impoverishment of the matrix in chromium in the neighbourhood of this point, and for this reason makes it less probable that the particle will grow sideways than that a new particle will form at a certain distance from the initial point of attack.

The second point to which we wish to direct attention is the presence along certain grain boundaries and certain twin boundaries of oxide-free bands, when the conditions of experiment are those of Region I (Fig. 3, Plate XVI). One might be tempted to explain the appearance of these bands by a local variation in the composition of the alloy. To explain the total absence of oxidation, however, this change would have to be considerable; it would, moreover, have to involve a layer of metal of the order of $1\ \mu$, since the oxide-free bands are frequently of this width. Further, it would be hard to explain the fact that the phenomenon occurs at least as often at the twinning planes as at the grain boundaries. It

would seem more reasonable to assume the existence of a competitive chemical process at the boundary of the two adjacent crystal lattices. We have made the following observations:

(a) The greater the difference in the number of oxide particles on the surfaces of two adjacent crystals, the more marked and the wider was the oxide-free band running along the boundary between them.

(b) The band always lay on the side of the grain (or twin) boundary corresponding to the crystal bearing the lesser number of oxide particles.

It seems probable that a metallic surface on which there is a strong tendency for oxide nuclei to form, exercises an attraction for oxygen beyond its own limits and that this is reflected in a slowing down of the reaction in a marginal zone, which is the wider, the smaller the tendency of the neighbouring surfaces to oxidize.

The third aspect which it is desired to discuss concerns the formation of surface relief effects on the metal, when operating under the conditions of Region III and, more especially, those of Region IV. The important point is that this phenomenon follows upon the selective oxidation of the alloy. Surface relief effects were, indeed, never observed after heating the alloy in a strictly neutral atmosphere (purified argon) or a reducing atmosphere (hydrogen), although tests were extended up to 1375°C . The only result of such treatments was to show up the grain boundaries by producing grooves with rounded edges, by a process previously described in connection with other metals and generally termed "thermal etching". The appearance of grain-boundary relief effects constitutes a phenomenon of a completely different nature and one which, in our opinion, can be related to selective oxidation in the following manner. During the selective oxidation of chromium certain chromium atoms are little by little removed from the crystal lattice of the alloy and transformed into Cr^{+++} ions which contribute towards the building up of a surface film of oxide. When the temperature is sufficiently high the lattice vacancies thus formed tend to fill up by migration of neighbouring atoms of nickel. A reorganization of the lattice thus takes place, as a result of which the metal surface is enabled to adopt the microgeometric profile corresponding to its state of minimum free energy.

It remains to explain why these surface relief effects which appear and persist in a slightly oxidizing atmosphere, disappear when the metal is heated in a reducing or neutral atmosphere. For this purpose it is necessary to bring in the surface film of chromium oxide. It has been possible to show by electron diffraction that the metal surfaces which develop striations of chemical origin are covered with a continuous film of oxide too thin to be perceptible under the microscope. This fact could not be demonstrated on specimens prepared under the conditions described earlier, for, as we have seen, such specimens exhibit, besides the regions covered with striations

and showing a metallic brilliance, randomly scattered islands of oxide. An electron beam impinging on such a surface gives the pattern of Cr_2O_3 , without its being possible to determine whether this is due in part to the metal surface free from compact oxide. To settle this point, as to whether an oxide film exists apart from the islands, it was therefore necessary to prepare a specimen oxidized under the same conditions but from which the islands of compact oxide had been eliminated. This was done by placing parallel to, and at a short distance from, the surface of the metal a sheet of iron or nickel on which the whole of the chromium oxide formed in the course of the experiment could condense. In this way a specimen was obtained which exhibited striations identical with those obtained by the method described above, but completely free from compact oxide. Although under the optical microscope the whole surface of the metal appeared to be equally brilliant, a very clear pattern of microcrystalline Cr_2O_3 was obtained by means of electron diffraction. This result is to be expected in view of the fact that under the conditions of the experiment the atmosphere is

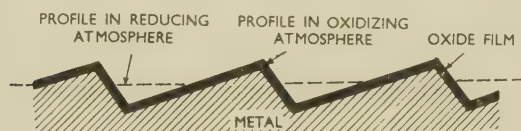


FIG. 18.—Schematic Representation of the Surface Profile of the Metal Produced by Treatment in Different Atmospheres.

largely oxidizing in respect to chromium. This experiment indicates that the specimen surface is not a free-metal/atmosphere surface but a metal/oxide interface. The data available on the surface tensions of molten metals suggest that the interfacial tension between solid metal and solid oxide must be lower than the surface tension of the metal under a hydrogen or argon atmosphere at the same temperature. It follows that the building up and the preservation of an equilibrium profile presenting geometrical forms characteristic of and conforming to the lattice structure of the metal, must be greatly favoured by the presence of a surface oxide film (Fig. 18).

When the experiment is carried out in an atmosphere of extremely pure hydrogen, the oxide film disappears and the surface tension of the metal is considerably increased. By reason of this, the profile just described becomes unstable and the atoms situated at the projecting edges tend to migrate to lower regions. The surface of the metal gradually levels out, with the exception of the intercrystalline grooves, the appearance of which is little affected in the course of all these treatments. The reappearance of striations when the specimen is once more subjected for a time to an oxidizing atmosphere does not conflict with this interpretation.

At first sight it may seem difficult to explain the reabsorption of the striations in pure argon at about

1200° C., as Cr_2O_3 does not undergo dissociation under these conditions. However, during the course of the research we have several times had occasion to note the marked tendency exhibited by thin films of chromium oxide to coalesce at such temperatures. As long as the alloy remains under a selective-oxidizing atmosphere this tendency is offset by the oxidation of fresh atoms of chromium which serve to maintain the continuity of the film on the surface of the metal. Under an argon atmosphere this mechanism no longer operates, so that after a certain time at 1200° C. in this gas the greater part of the surface of the metal becomes bare again. In this connection it is interesting to note that under similar conditions, striations due to light abrasion as well as those which result from bending are reabsorbed much less readily than those of chemical origin.

The phenomena of the formation of striations observed in the present work bear a close analogy to those previously noted by various authors on pure metals. Elam⁴ has recorded the formation of striations on the surface of copper, which had previously been oxidized, during heating *in vacuo*. She attributed this to selective oxidation along certain crystallographic directions, followed by dissociation of the oxide. Similar observations have been made on copper by Gwathmey and Benton⁵ and by Jacquet.⁶ Moreover, Shuttleworth, King, and Chalmers,⁷ on heating silver in air at 800° C., noted the appearance of striations on the surface very similar to those described here. After reviewing the various possible explanations, these authors suggest a modification of the free surface energy of the metal under the action of various gases, without indicating the exact nature of this effect.

The analogy between the features observed in the course of these different researches is so strong, and the similarity of the experimental conditions leading to their appearance or disappearance, so striking, that it is tempting to relate them to the same fundamental mechanism. Further experiments are needed, however, before applying to other systems the explanation which we suggest for the nickel-chromium alloys.

It would clearly be worth while to study more thoroughly than we have been able to do, the surface relief effects which are found on these alloys under the conditions outlined, with a view to securing information on the relative stability of the various crystal planes. It may be noted that the formation by selective oxidation of consecutive striations is dependent upon a factor which, at least to a first approximation, may be considered as isotropic, which is not the case for striations produced by mechanical stress. From the point of view of interpretation, therefore, the phenomena described in the paper seem to resemble more closely those to be observed during the growth of a metallic lattice from the vapour phase or by evaporation—both of which are operations at the moment technically impossible to realize with the alloys that form the subject of this study.

ACKNOWLEDGEMENTS

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REFERENCES

1. J. Moreau and J. Bénard, *Compt. rend.*, 1953, **237**, 1417.
2. J. Bardolle, *ibid.*, 1952, **234**, 2200.
3. J. Bardolle and J. Bénard, *Rev. Mét.*, 1952, **49**, 613.
4. C. F. Elam, *Trans. Faraday Soc.*, 1936, **32**, 1604.
5. A. T. Gwathmey and A. F. Benton, *J. Chem. Physics*, 1940, **8**, 431, 569; *J. Physical Chem.*, 1942, **46**, 969.
6. P. A. Jacquet, *Recherche aéronaut.*, 1951, (21), 35.
7. R. Shuttleworth, R. King, and B. Chalmers, *Nature*, 1946, **158**, 482.
B. Chalmers, R. King, and R. Shuttleworth, *Proc. Roy. Soc.*, 1948, [A], **193**, 465.

DISCUSSION *

DR. O. KUBASCHEWSKI † (Member): I have two small questions. One concerns the very first formation of the nuclei. There are theories that postulate the formation of monolayers a few ångströms thick, which may remain constant or may grow steadily. Are these nuclei formed at active centres, or is there a layer of a few ångströms, followed by coalescence and the formation of these observable nuclei?

My second question concerns the last stage of the process, particularly in these nickel-chromium alloys which are known to be very oxidation-resistant. Opinions are divided on whether it is the spinel or the chromic oxide or something else which protects the metal surface. It might be the spinel, but it could hardly be the pure chromic oxide. If it is a form of chromic oxide, it must contain nickel, which fills in some vacant sites. Have the authors any evidence for the composition or impurity content of the chromic oxide formed in their experiments?

The AUTHORS (*in reply*): As regards Dr. Kubaschewski's first question, it must be made clear first of all that the conditions under which the nuclei are formed depend to a very great extent on the operating temperature. This having been said, we believe that the mechanism of nucleus formation can be visualized in terms of observations recently made by

M. J. Bardolle on the oxidation of pure iron at about 850° C. under very low pressures of oxygen. In this case, where the phenomena are not as complex as in the nickel-chromium alloys, M. Bardolle observed, under certain conditions, the formation of nuclei similar to those described in the present paper, but it appears that a thin uniform film is always formed first; the nuclei form only at a second stage, as a result of coalescence of the initial layer. When the temperature is very high or when the oxidizing power of the atmosphere is sufficiently great, this coalescence takes place so rapidly that the first stage cannot be detected. Moreover, on examination at high magnification, the films exhibit interference colours, similar to those referred to in the present paper, and it is found that the films very often have a granular structure. This structure would represent the first indication of the tendency to coalescence.

Our investigations have not yet proceeded far enough to enable us to give a definite reply to the question concerning the constitution of the oxide film. We believe, however, that the presence of small quantities of Ni²⁺ ions in the Cr₂O₃ lattice, if they exist, could not be revealed directly by electron-diffraction examination of the oxide films, because of the limited precision of this method in making lattice-parameter measurements.

* Remarks contributed on the occasion of the presentation of the paper at a joint meeting of the Institute and the Société Française de Métallurgie held in London in April 1954.

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1572 DIFFUSION OF NITROGEN AND OXYGEN IN TITANIUM*

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SYNOPSIS

The diffusion rates in massive β -titanium, and their temperature-dependence, have been determined for nitrogen in the range 900°–1570° C. and for oxygen in the range 950°–1414° C., assuming D to be independent of the solute concentration. This appears probable in the case of nitrogen throughout the solubility range in β -titanium; diffusion rates for oxygen, however, appear to decrease at higher solute concentrations.

A mathematical analysis has been carried out to account for the initial deviation from the parabolic rate law in gas/metal reactions. An approximately linear reaction rate has been derived for short reaction times.

The case of diffusion with simultaneous formation and growth of a thin surface layer has also been analysed. An expression has been derived permitting approximate calculation of the diffusion coefficient of the solute in the surface layer from obtainable experimental data, when the layer is too thin for experimental determination of the concentration distribution. This analysis was used to evaluate the diffusion coefficients of nitrogen in α -titanium and titanium nitride between 900° and 1570° C.

I.—INTRODUCTION

THE contamination of titanium by nitrogen and oxygen during working and shaping operations is of considerable importance in view of the marked effect of both these elements on the properties of the metal. In general, only a superficial contamination may be tolerated. A knowledge of the diffusion rates of nitrogen and oxygen in massive titanium is, in consequence, of immediate practical interest in the evaluation of the extent of contamination by these elements during any working of the metal. An investigation of the diffusion rates of these interstitial solutes was therefore considered desirable.

No work on diffusion in titanium has previously been reported, except for the calculation of the diffusion coefficient for oxygen in α -titanium carried out by Alexander and Pidgeon.¹ The value of the diffusion coefficient reported, of the order of 10^{-7} cm.²/sec., in the temperature range 463°–565° C., seems unexpectedly high. The authors' method of calculation, however, involved the assumption of homogeneous diffusion of oxygen taking place in titanium throughout the concentration range 0–66.7 at.-% oxygen. In view of the known existence of a number of intermediate structures at lower oxygen concentrations,² this assumption over-simplifies the problem, and calculations based on it are unlikely to be accurate.

The reactions of titanium with oxygen have been stated by different investigators to obey the parabolic,³ linear,⁴ and logarithmic^{1, 5} rate laws. Parabolic³ and linear⁶ rates have been reported for

reactions between titanium and nitrogen. The two gases have been found to react readily with titanium at elevated temperatures, the reaction rates of oxygen being considerably higher than those reported for nitrogen.

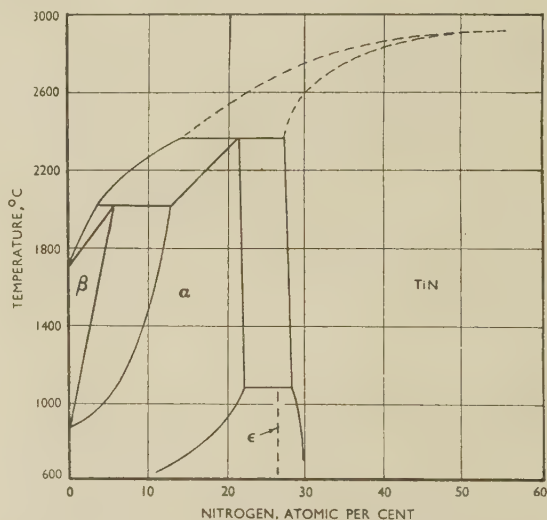


Fig. 1.—Partial Titanium-Nitrogen Equilibrium Diagram.⁷

The data available on the two binary systems of interest,⁷ shown in Figs. 1 and 2, indicate that homogeneous diffusion is unlikely to take place in reactions of titanium with nitrogen or oxygen. These reactions can be expected to result in the formation and growth with time of one or more surface layers, corresponding to the intermediate phases existing in the appropriate

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system at the reaction temperature. The diffusion in both the α and the β structures will probably be interstitial. That in the intermediate structures, however, is more likely to take place by vacancy migration, since both the nitride and the known oxide structures have been stated to possess large numbers of vacant sites.² Furthermore, the diffusion rates in the relatively open, body-centred cubic β structure may be expected to be much higher than those in the close-packed α . Consequently, the thickness of the surface layer formed during the diffusion may well be small compared with the penetration of the solute into the core of the specimen, should the latter be originally in the β condition. It was therefore believed that the

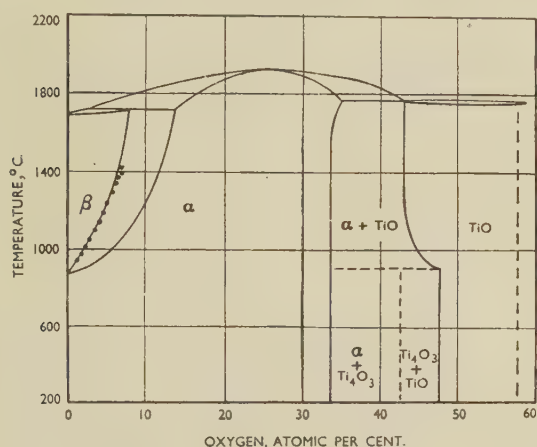


FIG. 2.—Partial Titanium-Oxygen Equilibrium Diagram.⁷

introduction of the solute into the metal by means of direct gas/metal reactions would provide a convenient means of preparing diffusion specimens.

II.—EXPERIMENTAL METHOD

Argon-arc-melted iodide titanium was used throughout this investigation. It was necessary to keep the amount of working of the metal to a minimum, in order to avoid accumulated contamination effects. Hence the use of wire, or of spherically shaped specimens, although convenient from the point of view of the mathematical analysis, was precluded. The melted button was therefore hot-forged and rolled, and then swaged cold to 0.375-in.-dia. rod, from which cylindrical specimens 0.350 in. in dia. and 45 mm. long were afterwards machined. The metal was 99.85+ % pure, the main impurities being carbon 0.036, manganese 0.03, oxygen 0.011, and aluminium 0.01 %. The high purity of this material was indicated by the hardness, as vacuum-annealed for 1 hr. at 750° C., which varied between 58 and 64 D.P.N. (10-kg. load).

Each specimen was first abraded under purified kerosene on silicon carbide paper down to No. 600, washed with water and detergent, then washed with acetone and immediately inserted into the reaction vessel, which was then evacuated. For reactions above 1000° C. the specimens were heated to the

reaction temperature required, and the reaction was started after this temperature had been maintained constant for 30 min. This length of time was considered sufficient to ensure that the temperature of the specimen was substantially the same as that indicated by the external thermocouple. Specimens to be reacted at temperatures below 1000° C. were annealed *in vacuo* at 1000° C. for 1 hr. after the initial surface preparation. The reaction vessel was then cooled to the reaction temperature required, and the reaction begun after equilibrating for 30 min.

The gas/metal reactions were carried out in a modified Sieverts apparatus. The reaction vessel, of Vycor (96% silica) glass, or mullite, according to whether the reactions were below or above 1000° C., could be evacuated and maintained under vacuum by means of a two-stage mercury-condensation pump. The reaction temperature was measured by means of calibrated Chromel/Alumel or platinum/platinum-10% rhodium thermocouples, and maintained constant within $\pm 2^\circ$ C. in diffusion runs at temperatures up to 1000° C. and within $\pm 5^\circ$ C. above that temperature. The effective reaction volume was measured with pure argon, and the appropriate gas then admitted. Whenever possible, the reaction rates were followed by observing the pressure changes in the known reaction volume, the pressure being kept within $\pm 5\%$ of the nominal value by suitable additions of small quantities of gas during the reaction.

Initially, a few experiments had been carried out using high-purity oxygen, obtained by thermal decomposition of potassium permanganate and subsequently passed through Drierite and magnesium perchlorate traps. The observed reaction rates did not differ to any significant extent whether this high-purity oxygen or commercially pure, dried cylinder oxygen was used. In view of the difficulties involved in the production of the oxygen from permanganate, it was decided to use the "pure grade" cylinder oxygen. The traces of nitrogen and argon present as impurities were not considered significant. The nitrogen used was also obtained commercially, and the cylinder gas was further purified by passing it through either a liquid-nitrogen trap or through a tube furnace filled with titanium turnings maintained at 650° C. No difference was observed in the reaction rates whichever method of purification was used. The small amount of argon present as a natural impurity in the gas was considered of no significance.

After the completion of each diffusion run, two lengths of approximately 6 mm. were cut off from each end of the diffusion specimen, leaving a length possessing a solute-concentration gradient solely due to radial diffusion, provided that the time of the diffusion was suitably controlled. The surface layers of the reaction products were then machined off, and six to eight analytical samples (in the form of chips) were turned from the remaining core of the specimen. From these the radial solute-concentration distribution could be determined. The analysis for nitrogen was carried out by a modified Kjeldahl method, and

in order to prevent the evolution of free nitrogen the samples were dissolved slowly in 10% H_2SO_4 solution, with selenium sulphate as catalyst. Vacuum-fusion analysis, with addition of tin,⁸ was used for the oxygen determinations, which were conducted in a commercial vacuum-fusion unit.

The mathematical analysis of the data thus obtained was carried out on the basis of the solution of Fick's diffusion equation for an infinite cylinder, with the diffusion coefficient assumed constant, as reported recently in an investigation of the diffusion of nitrogen in zirconium.⁹ To neglect the surface layers formed results in a relatively small error, provided that their thickness is small compared with the radius of the specimen, and therefore they were not taken into consideration in this analysis.

III.—EXPERIMENTAL RESULTS

1. NITROGEN

The rates of reaction were investigated between the limits 800° and 1400° C. It was found that the rates throughout this temperature range were in accordance with the parabolic law, but that deviations from the ideal law were present during the initial reaction period. These initial deviations became apparent when the amount of the gas absorbed was plotted against the reaction time on a log-log basis (Fig. 3, Curve A). The slope of the plot is approximately equal to $\frac{1}{2}$ for higher values of t , but initially the slope was considerably steeper and varied between 1.0 and 1.5. An attempt to account for this type of deviation has been made, and is presented below. What appears to be a slightly different type of deviation was

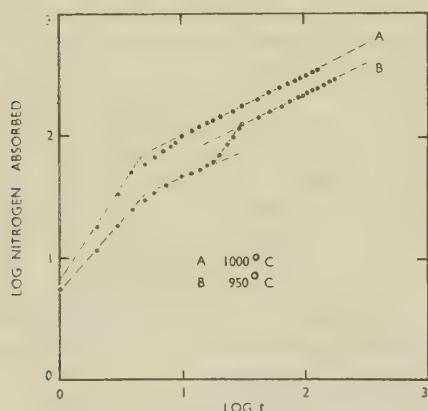


FIG. 3.—Initial Deviations from the Parabolic Rate Law in Reactions of Titanium with Nitrogen.

observed in a few runs (Fig. 3, Curve B). However, this is probably identical with the first type of deviation, being due to the rupture of the surface layer in course of formation, with consequent exposure of the metal beneath.

The parabolic rate constants have been calculated from the reaction data for $t > 60$ min., in order to avoid the errors due to the initial deviations. $\log k$

was then plotted against the reciprocal temperature (Fig. 4). The equation for the temperature variation of the parabolic rate constant k ((ml. S.T.P./cm.²)²/

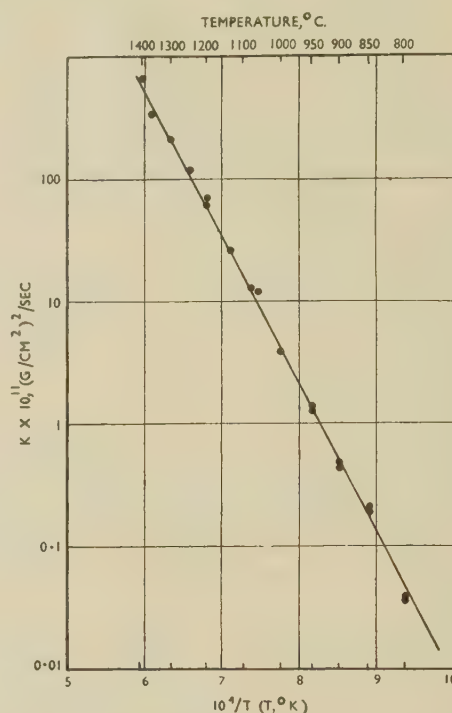


FIG. 4.—Variation with Temperature of the Parabolic Rate Constant in the Reactions of Titanium with Nitrogen.

sec.) obtained from this plot by the method of least squares was :

$$k = 3.3 \times 10^{-2} \exp \left\{ - \frac{53,800 \pm 1500}{RT} \right\}$$

The energy of activation of the reaction during the initial period of deviation from the parabolic rate law was also calculated, using the expression (see Appendix, p. 101) :

$$V = Zt \exp(-Q/RT)$$

where Z is the number of collisions/cm.²/sec., t the time of reaction (sec.) during which an approximately linear rate was observed, and V the amount of the gas absorbed per unit surface area of the specimen. The value of Q thus found was $41,300 \pm 4000$ cal. Owing to the very low precision of the initial readings, and to the unknown effect of the initial rapid reaction rates on the local temperature of the surface of the specimens, this value must be considered as a rough approximation only. It is worth noting, however, that this value is not in agreement either with the activation energy for long-time surface reaction, or with the activation energy obtained for the diffusion of nitrogen in β -titanium (see below).

Except for the specimens reacted at or below 850° C., a golden-coloured film of titanium nitride was visible after the reactions. The nitride layers were also formed at 850° and 800° C., as indicated by the microscopic examination of the end sections. This

nitride layer was adherent, very hard and brittle. No detectable decomposition of the nitride took place *in vacuo* at temperatures up to 1400° C., this observation being consistent with the known difficulty of analysing the nitrogen content of titanium by the vacuum-fusion method.⁸ The effect of decrease in

tion was made in the mathematical analysis for the reduction of the radius due to the growth of the surface layers. The values of the diffusion coefficient shown in Fig. 8 were obtained by using two separate lots of iodide metal, and, as can be seen, are in good agreement. From the experimental data the equation:

$$D_{\beta} = 3.5 \times 10^{-2} \exp \left\{ - \frac{33,800 \pm 1400}{RT} \right\}$$

was obtained for temperatures between 900° and 1570° C. No significant variation of the diffusion coefficient was found to result from decreasing the nitrogen pressure, the multiplicate values at 1200° C. having been obtained at pressures varying from atmospheric down to 10 mm. Hg.

An attempt was made to calculate the approximate values of the diffusion coefficients for nitrogen in α -titanium from the data secured during the investigation of β diffusion. The approximate mathematical treatment permitting this is presented in the Appendix. The following equation was obtained:

$$D_{\alpha} = \frac{d_{\alpha}}{2.824t} \left\{ \left[\frac{c_i^{\alpha} + 0.452(c_o^{\alpha} - c_i^{\alpha})}{c_o^{\alpha} - c_i^{\alpha}} \right] d_{\alpha} + 0.5 \frac{c_o^{\beta}}{c_o^{\alpha} - c_i^{\alpha}} \sqrt{\frac{D_{\beta} t}{a^2}} \right\}$$

where d_{α} = thickness of the α surface layer, t = time of diffusion, c_i^{α} = minimum concentration of nitrogen in the α phase at the diffusion temperature, c_o^{α} = maximum concentration of nitrogen in the α phase at

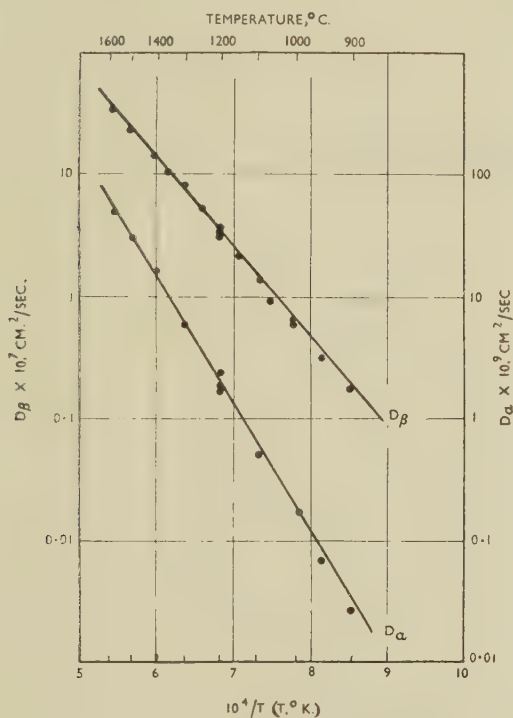


FIG. 8.—Variation with Temperature of the Diffusion Coefficients of Nitrogen in α - and β -Titanium Above the Transformation Temperature.

pressure was to increase the reaction rate slightly, but no quantitative relationship between the pressure and reaction rates has been established.

During investigation of the diffusion of nitrogen in β -titanium, the formation of two surface layers was observed in all the specimens reacted above 950° C. These were identified as the nitride (thin, outer layer) and the α phase (inner layer), surrounding a core which at the diffusion temperature remained throughout in the β condition, as illustrated in Fig. 5 (Plate XIX). At 950° C., however, another layer (Fig. 6, Plate XIX) was observed, apparently subdividing the α layer. On the basis of the most recent data on the system,⁷ this appears to be the phase designated ϵ . A triple layer, however, was also observed in specimens reacted below the transformation temperature, as shown in Fig. 7 (Plate XIX). Since the core then remained in the α condition throughout, the available data on the titanium-nitrogen equilibrium diagram below the transformation temperature are insufficient to permit complete interpretation of the surface-layer structures present.

In all the specimens analysed for the diffusion data the total thickness of the surface layers formed was less than 3% of the cylindrical radius, and no correc-

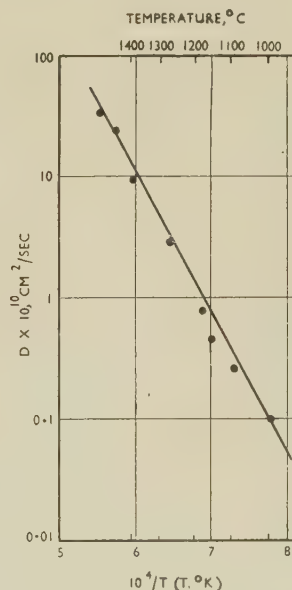


FIG. 9.—Variation with Temperature of the Diffusion Coefficients of Nitrogen in Titanium Nitride.

the diffusion temperature, c_o^{β} = surface concentration of nitrogen in the β phase, as obtained by extrapolation during investigation of β diffusion, D_{β} = diffusion coefficient for nitrogen in β -titanium, a = original specimen radius.

The values of the diffusion coefficients calculated from this equation for different temperatures are shown in Fig. 8. The data appear consistent, and the temperature variation of the diffusion coefficient was found to conform to the equation:

$$D_{\alpha} = 1.2 \times 10^{-2} \exp \left\{ - \frac{45,250 \pm 2250}{RT} \right\}$$

throughout the range 900°–1570° C. At 950° C. and below, however, the diffusion coefficient was calculated for the inner α layer only. A corresponding calculation for the total α thickness, including the ϵ layer, indicated that the diffusion rates may be significantly different at higher nitrogen concentrations.

The mean diffusion coefficient of nitrogen in the nitride layer formed during the reaction (D_{γ}) was calculated, as shown in the Appendix, by an extension of the analysis used for calculating D_{α} . The values obtained are shown in Fig. 9. The equation for the variation with temperature of the diffusion coefficient was:

$$D_{\gamma} = 5.4 \times 10^{-3} \exp \left\{ - \frac{52,000 \pm 3500}{RT} \right\}$$

2. OXYGEN

It was found in the preliminary experiments that the rates of reaction increased rapidly at temperatures above the transformation temperature of the pure metal, and that maintaining atmospheric pressure of oxygen in the reaction vessel at all the temperatures investigated caused the formation of excessively thick surface layers of the transformed α and intermediate oxide phases. Since the success of the mathematical method of analysis used depends on the thickness of the surface layers being slight, it was decided to admit only a predetermined quantity of oxygen into the reaction volume, and to let the reaction take place at decreasing pressure of oxygen, as in a previous investigation of the diffusion of hydrogen in α -titanium.¹⁰

The diffusion of oxygen in β -titanium was investigated throughout the range 950°–1414° C., at intervals of approximately 50° C. The amount of oxygen admitted at all temperatures was calculated to correspond to full saturation of the β phase, on the basis of the then-published data.¹¹ During the diffusion run only part of this amount of gas diffused into the β phase, as the relative saturation, approximately calculated for $Dt/a^2 = 0.04$, would be only of the order of 50%. The remaining oxygen was therefore expected to produce a transformed α layer. It was found, however, after initial experiments at 1400° C., that no α or intermediate oxide layers were present after a reaction time of 1 hr. Assuming the solubility data used to be correct, a diffusion coefficient of the order of 2×10^{-5} cm.²/sec. was indicated, and this was considered exceedingly high. The amount of oxygen initially admitted was therefore increased, and the time of reaction halved, as the accuracy of the solubility data appeared doubtful

on the basis of more recent work.⁷ A transformed α layer was then obtained, and the mathematical analysis carried out in the usual way.

The experimental values for the diffusion coefficients at various temperatures are shown in Fig. 10, and the temperature-dependence of the diffusion coefficient was found to be:

$$D_{\beta} = 1.6 \times \exp \left\{ - \frac{48,200 \pm 3200}{RT} \right\}$$

The extrapolated values of the maximum solute concentration in the β phase, i.e. the surface concentration values, shown in Fig. 2, were in good agree-

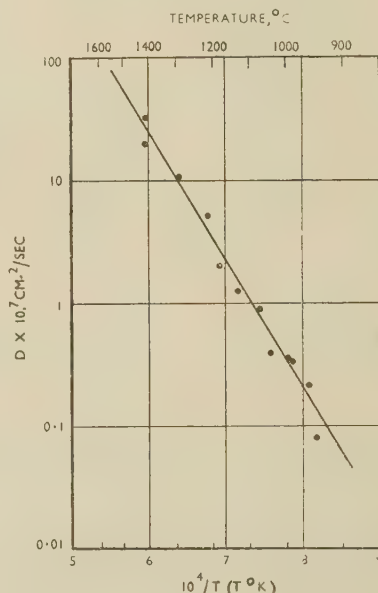


Fig. 10.—Variation with Temperature of the Diffusion Coefficients of Oxygen in β -Titanium.

ment with those reported.⁷ Above approximately 1200° C. these values are appreciably higher than those given by Bumps, *et al.*,¹¹ and the solubility of oxygen in β -titanium is shown to increase with temperature, instead of remaining substantially constant.

IV.—DISCUSSION OF RESULTS

1. GENERAL

The mechanism of diffusion in the solid state is still largely a matter of speculation. It has been shown¹² that in substitutional diffusion the change in the local concentration with time is the result of two opposite flows of the solute and solvent atoms. Hence, in order to represent the phenomenon, two separate diffusion coefficients must be taken into consideration. Interstitial diffusion, on the other hand, can be considered as the flow of the solute atoms through the fixed solvent lattice. Any effects of the movements of the solvent atoms, whether due to their migration, or to the dimensional changes in the lattice caused by diffusion, are of an order of magnitude small in com-

parison with those caused by the flow of the solute atoms. Thus, only one diffusion coefficient is necessary in the mathematical analysis of the phenomenon.

Little is known at present about the state in which the solute atoms exist in the interstitial solution. It has been stated,¹³ on the basis of the solute migration in an electric field, that hydrogen exists in solution in the form of protons, while both nitrogen and oxygen are present as negatively charged ions. The experimental evidence on which the latter statement is based has not been confirmed however. From consideration of the respective sizes of the interstitial holes, and the atomic and ionic radii of the possible interstitial solutes, it appears unlikely that this is a true representation of the state within the solution. In general, hydrogen diffuses very rapidly through the metal lattices, while nitrogen and carbon diffuse at rates about two to three orders of magnitude slower, and oxygen at rates intermediate between those of the other interstitial and the substitutional solutes. This may be interpreted as indicating that the hydrogen diffuses in the form of protons, but no conclusions can be drawn as to the state of the hydrogen when it is actually occupying an interstitial position. Nitrogen and oxygen, on the other hand, may well be present in the interstices as negatively charged ions, as indicated by the enormous increase in hardness of titanium metal on addition of small amounts of these elements, consistent with high bond strength and possibly considerable lattice strains; but it is more probable that they diffuse in atomic form. Otherwise, the activation energies for diffusion of these elements would be expected to be considerably higher than those actually observed, in view of the drastic polarization of the solute ion necessary if it were to migrate from one interstitial position to the neighbouring one. Furthermore, diffusion of nitrogen might then be expected to be markedly slower than that of oxygen, since the N^{-3} ion, radius 1.70 Å., is considerably larger than the O^{-2} ion, radius 1.32 Å.¹⁴

The data available, however, do not permit a determination of the state of either the nitrogen or the oxygen atoms when in an α - or β -titanium lattice. The metallic characteristics of the nitride and the monoxide of titanium indicate that these structures are not ionic. The isomorphism of these two structures with that of titanium carbide, and the existence of solid pseudo-binary and pseudo-ternary solution within wide ranges of the TiN-TiC-TiO system indicate further that the bond is a complex one, as discussed recently by Nowotny.¹⁵

2. NITROGEN

The problem of the initial deviation in the diffusion-controlled reactions is considered in the Appendix. From the data obtained in this work it appears that while the long-time rates are controlled by the diffusion through the nitride layer, the initial controlling process is more likely to be the diffusion through the α structure. Consequently, it may be concluded that the formation of the α transformed

layer is almost instantaneous, but that the nitride begins to form only after the reaction has been in progress for an appreciable time.

A typical comparison between the experimental data and the theoretical curve of best fit is shown in Fig. 11. The agreement between the theoretical and experimental data is in all cases very good, and it is thought that no appreciable variation of the diffusion coefficient occurs throughout the solubility range of nitrogen in β -titanium. The extensive solubility range of nitrogen in α -titanium, and the uncertainty as to the number of phases formed at increasing concentrations of nitrogen in the metal, make the experimental determination of the diffusion coefficients difficult. Two experiments carried out, respectively,

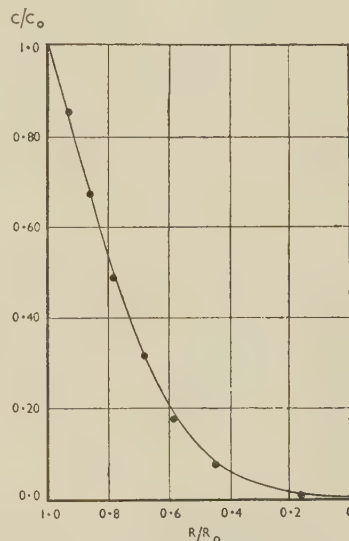


Fig. 11.—Typical Comparison Between the Experimentally and Theoretically Determined Distribution of Nitrogen in a Diffusion Specimen. 17 hr. at 1080° C. Theoretical curve for $Dt/a^2 = 0.04$.

at 850° and 825° C. resulted in concentration/distribution curves not in agreement with the theoretical solutions. Furthermore, the surface layers formed (Fig. 7, Plate XIX) were not in agreement with the most recent data available on the system. Semi-quantitatively, the diffusion coefficient appears to be concentration-dependent, decreasing at high nitrogen concentrations. The method of analysis used in this work for the calculation of the diffusion coefficients is only approximate, but the data obtained are consistent, and the values appear reasonable. The calculated values correspond to low nitrogen concentrations, not exceeding about 7 at.-%, where the variation of the diffusion coefficient appears to be slight.

It is suggested that in order accurately to determine the diffusion rates of nitrogen in α -titanium the use of diffusion couples, composed of pure metal and titanium nitride, and the subsequent Matano analysis of the concentration distribution would be necessary. By this method the concentration dependence of D_α

could be investigated directly, the validity of the approximate values obtained in this work checked, and the presence of any intermediate phases readily determined.

The diffusion of nitrogen in the nitride is not interstitial, and the diffusion coefficients obtained by the method of calculation used represent only the overall result of the nitrogen flow inwards and the titanium flow outwards. It is quite probable that the latter contributes appreciably to the overall result. The calculated values thus correspond to the "chemical-diffusion coefficient".¹² Furthermore, in addition to the solubility of nitrogen in the α phase, data on the composition range of the nitride are also required. The extent of this range is at best only tentative. However, by varying it within reasonable limits, relatively small variation was obtained for the values of D_v . A more significant error is thought to have been caused by the uncertainty in the measurement of the thickness d_v , which varied between 2 and 20 μ . Although the calculated values, as indicated in Fig. 9, are in reasonably good agreement, they are considered to be within the right order of magnitude only.

3. OXYGEN

The high reaction rates and the rapid formation of thick surface layers during the reactions indicate that the difference between the diffusion rates in the two titanium metal structures is considerably less with oxygen than was the case with nitrogen. From calculations based on the data of Jenkins¹⁶ it appears that the diffusion rates of oxygen in α -titanium are approximately 10^{-10} and 10^{-9} cm.²/sec. at 700° and 800° C., respectively, i.e. of the same order of magnitude as the diffusion rates in β -titanium extrapolated to these temperatures. Thus, given an unlimited supply of oxygen, the effective penetration of the solute in the α , and perhaps also in the oxide surface layers, can no longer be considered negligible in comparison with the penetration into the β core. No data could be obtained from these experiments on the diffusion in the α phase, since the approximate mathematical analysis derived does not apply, in view of the variable surface concentration. The rough approximation of the surface-reaction rates, as obtained by the determination of the reaction rates at decreasing pressure, indicates that the activation energy of the reaction at temperatures above 900° C. is of the order of 100,000 cal. This value is not in agreement with any published data for reactions of titanium with oxygen. However, in a recent investigation of the oxidation rates of zirconium,¹⁷ the activation energy of the reaction with β -zirconium at high temperatures was found to be 112,000 cal., although the analysis indicated lower activation energies in lower temperature ranges. It is therefore thought that in the case of titanium also the overall reaction may well be controlled by different processes below and above approximately 950° C. In view of the number of intermediate structures existing in the titanium-oxygen system, and the attendant complications

caused in the reaction by the presence of a number of surface layers and interfaces, this conclusion appears reasonable. No data, however, are so far available to permit the determination of the controlling processes at any of the temperature ranges investigated.

In discussing the diffusion of oxygen in β -titanium, it must be pointed out that the agreement with the theoretical concentration-gradient values was in this case not as good as in the case of nitrogen. A typical theoretical curve of best fit chosen for a set of experimental data is shown in Fig. 12. Two features are obvious on comparing the two curves. First, the relative concentration values at low R/R_0 are higher than the corresponding theoretical values. Secondly, and more marked, there appears to be a local flattening

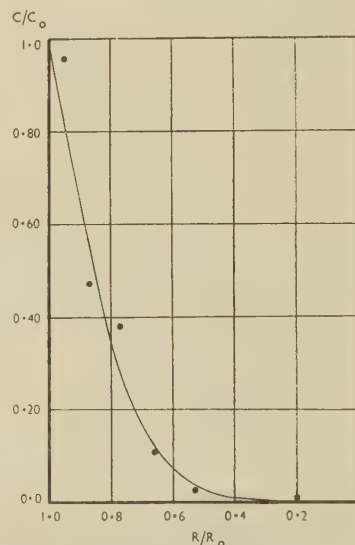


Fig. 12.—Typical Comparison Between the Experimentally and Theoretically Determined Distribution of Oxygen in a Diffusion Specimen. 30 min. at 1414° C. Theoretical curve for $Dt/a^2 = 0.02$.

in the experimental curve, at comparatively high values of c/c_0 and R/R_0 . Both these observations applied to all the experimental diffusion specimens, and the latter discrepancy is well beyond the limits of analytical error. The local flattening of the concentration/distribution curve is believed to be due to thermal effects arising during the initial stages of the reactions. The temperature rose during the first minute of the reaction, as indicated by the external thermocouple. Since the heat of the oxidation reaction is 220,000 cal.,¹⁸ it is thought that the temperature of the specimen surface may have increased very considerably at that time. In the early stages of the reaction, therefore, the solute may well have diffused at comparatively high rates into the specimen: in addition, the maximum solubility c_0 at this increased temperature would have been higher than that corresponding to the nominal reaction temperature. In consequence, when the reaction slowed down and the surface temperature fell to nominal, the concentration distribution in the specimen was

different from that assumed in the mathematical analysis. Further diffusion taking place with this initial variation in local concentration may well result in the observed interruption in the experimental curve.

The values of the diffusion coefficients were determined on the assumption of no dependence on the solute concentration. Attempts to analyse the data in terms of a solute-concentration dependence were unsuccessful. The D values, therefore, represent only approximate diffusion rates, since there exist indications that the coefficients vary significantly with the solute concentration within the solubility range investigated. The diffusion rates appear to decrease with an increase in the solute concentration.

APPENDIX

1. SURFACE REACTION RATES IN DIFFUSION-CONTROLLED REACTIONS

The parabolic reaction rates have been generally derived on the assumption of diffusion control of the overall reaction. Considering the case of unidirectional diffusion into a semi-infinite solid, the initial and boundary conditions are:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad x, t > 0$$

$$c(x, 0) = c_i; \quad c(0, t) = c_o; \quad D = \text{const.}$$

and the solution of the problem is given by:

$$\frac{c - c_i}{c_o - c_i} = \text{erfc} \left(\frac{x}{2\sqrt{Dt}} \right) \quad (1)$$

A concentration-independent diffusion coefficient D and a discontinuous change in the solute concentration at the diffusion interface are assumed in deriving this solution. Integrating (1), we obtain:

$$\begin{aligned} V &= \int_0^\infty (c - c_i) dx = (c_o - c_i) \int_0^\infty \text{erfc} \left(\frac{x}{2\sqrt{Dt}} \right) dx \\ &= 2(c_o - c_i) \sqrt{\frac{Dt}{\pi}} \quad (2) \end{aligned}$$

giving the total amount of the solute reacted/cm.², V , as proportional to $t^{1/2}$. It is evident that, differentiating this equation with respect to time, we obtain reaction rates becoming infinitely large as t tends to zero. However, the rate of supply of the gas to the metal surface is determined by the pressure, temperature, the molecular weight of the gas, and the activation energy value of the surface reaction. The rate determined by these variables is finite, and cannot be exceeded at any time during the reaction. Hence the assumption of the discontinuous solute-concentration change, used in the above derivation, does not in practice apply, and an initial deviation from the parabolic law may be expected, at least until the time when the surface concentration of the solute reaches the theoretical value c_o .

In order to analyse the problem, let us define, in

analogy with heat-flow problems,¹⁹ the boundary conductance h , and state the problem conditions as:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad x, t > 0$$

$$c(x, 0) = c_i; \quad \frac{\partial c(0, t)}{\partial x} = h(c_o - c_i'); \quad D = \text{const.}$$

where c_i' is the surface solute concentration at time t , and other symbols have the same meaning as previously. The solution of this problem is given by:¹⁹

$$\begin{aligned} \frac{c - c_i}{c_o - c_i} &= \text{erfc} \left(\frac{x}{2\sqrt{Dt}} \right) \\ &\quad - \exp(hx + h^2Dt) \text{erfc} \left(\frac{x + 2hDt}{2\sqrt{Dt}} \right) \quad (3) \end{aligned}$$

the surface concentration consequently being:

$$\frac{c - c_i}{c_o - c_i} = 1 - \exp(h^2Dt) [\text{erfc}(h\sqrt{Dt})] \quad (4)$$

which, for small values of $h\sqrt{Dt}$ reduces to:

$$c(0, t) = c_i + (c_o - c_i)[1 - \exp(h^2Dt)] \quad (4a)$$

Note that the theoretical surface-concentration value c_o is never actually reached, but for large values of h^2Dt the error involved in assuming this value is negligible.

To find the total amount of gas reacted in time t , we can integrate equation (3) and obtain:

$$V = \frac{2(c_o - c_i)}{h} \left[\frac{h\sqrt{Dt}}{\sqrt{\pi}} - \text{erf} \frac{h\sqrt{Dt}}{2} \right] \quad (5)$$

The amount of the gas reacted per unit surface area is not here related to the reaction time as simply as in the case of equation (2). Mathematical analysis indicates that the total gas reacted at $t \rightarrow 0$ is proportional to $t^{3/2}$. For large values of t —or rather of the parameter h^2Dt —the reaction rate does not differ significantly from that given by equation (2), but the total gas absorbed is decreased by an amount depending on the value of h . At intermediate values of the parameter the amount absorbed is, to a first approximation, directly proportional to h^2Dt .

The physical significance of the boundary conductance h lies in the limitation of the maximum possible diffusional flow rate across the gas/solid interface. This term should probably include a factor corresponding to the boundary conductance proper, varying from zero to unity, which may or may not be temperature-dependent. The other factor is that depending on the rate of supply of the gas to the interface, of the form $Z \times \exp(-Q/RT)$, where Z is the number of collisions/cm.²/sec., and Q the activation energy of the surface reaction. If the former factor is assumed to be of the order of unity in the case of the highly reactive titanium, then for the initial period of reaction, where the rate law is approximately linear, the volume of the gas reacted will be given approximately by:

$$V = Zt \exp(-Q/RT)$$

and the activation energy Q can be calculated from the known data of the volume absorbed against time, since Z can easily be evaluated.

When there is no surface-layer formation, the value of h may be determined, provided D and t are known. Differentiating equations (2) and (5) we obtain:

$$\frac{\partial V(\text{ideal})}{\partial V(\text{experimental})} = \left\{ 1 - \exp \frac{h^2 D t}{4} \right\}^{-1}. \quad (6)$$

Hence, from the slopes of the ideal (equation (2)) and experimental plots of the total gas absorbed against time, it may be possible in some cases to determine the approximate value of the parameter $h^2 D t$, and hence the value of h .

The derivation of equation (6) does not apply in the case of a gas/solid reaction accompanied by the formation and growth with time of a surface layer of a new phase. While the initial deviation from the parabolic rate law can still be expected to take place, the long-time parabolic rate will no longer be that corresponding to the initial conditions of the reaction. Consequently, no quantitative comparison between the initial and the final rates in these reactions can in general be carried out.

2. DIFFUSION WITH THE FORMATION OF A SURFACE LAYER OF INCREASING THICKNESS

The method of analysis applied to the determination of the diffusion coefficients of nitrogen and oxygen in β -titanium can be used only for the coefficient in the core of the specimen, and a determination of the concentration distribution by chemical methods is necessary in order that the mathematical analysis be rendered possible. The growing nitride and transformed α layers were too thin to permit chemical analysis of the concentration gradient in them. Approximate values of the diffusion coefficients in these layers may be obtained, however, by mathematical analysis. Although the titanium-nitrogen system is used in this derivation, the results apply to any similar binary diffusion system.

(a) Qualitative

Consider a binary system of the titanium-nitrogen type, as shown in Fig. 13. A specimen containing c_i^β of the solute heated to a temperature T , above the transformation, consists solely of the β phase. This phase cannot accommodate more than c_o^β of the solute, and when the external gas pressure is lower than, or equal to, that in equilibrium with the saturated β phase, a continuous concentration-gradient variation will be obtained in the diffusion specimen. If, however, the external gas pressure is higher than that equilibrium value, the surface concentration must be higher than the maximum solubility in the β phase. The formation of heterogeneous regions necessary for a continuous change of solute concentration is impossible on thermodynamic grounds, as first pointed out by Rhines.²⁰ Therefore

an α layer will begin forming as soon as the surface becomes saturated, provided that the rate of supply of solute is sufficiently high. The solute absorbed from now on will be distributed partly to supply the growth inwards of the α layer, and partly diffusing

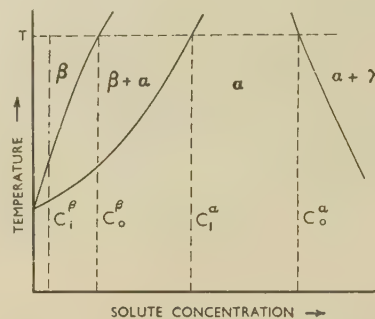


Fig. 13.—Equilibrium Diagram of a Binary System in Which Surface Layer Formation Can be Expected to Occur During Reaction of Pure Components.

across the interface into the β core. Thus, there will be discontinuities in the solute concentration at the interface of the phases formed during the diffusion, as schematically shown in Fig. 14. The limiting concentrations c_o^α and c_i^β are probably both given fairly accurately by the maximum solubility in the α phase,

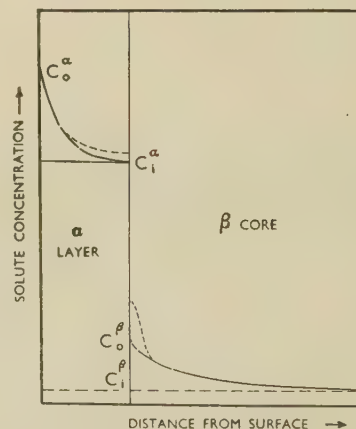


Fig. 14.—Schematic Representation of the Solute Concentration Distribution in the α and β Phases.

and the initial solute content, respectively. However, both c_i^α and c_o^β are likely to be higher than the equilibrium values, as some degree of supersaturation may be necessary in order that the transformation should begin.

The α structure being close-packed, while the β is body-centred cubic, diffusion in the latter can be expected to be one or more orders of magnitude more rapid than that in the former. If we consider, therefore, only the case of the formation of the α layer, then the growth of this surface layer should be very slow as compared with the rate of the solute penetration into the β core. The following analysis concerns a problem of this type.

(b) Quantitative

For the purposes of the quantitative analysis of the problem, the following assumptions are made:

(i) The diffusion in both phases obeys Fick's law, D being independent of solute concentration.

(ii) The interface does not affect the diffusion process.

(iii) The maximum and minimum solute concentrations in the surface layer correspond to the equilibrium values at the diffusion temperature.

(iv) The maximum solute concentration in the β core is the value of c_o^β , as extrapolated in the previous investigation (i.e. the maximum solute solubility in the β phase at the diffusion temperature).

(v) The diffusion across the gas/metal interface can be treated as diffusion into the α phase at minimum solute concentration, i.e. c_i^α .

To simplify the analysis, only the case of $D_\alpha \ll D_\beta$ will be considered. In this case, for small time, t , the thickness of the surface layer is very small. Consequently the original specimen surface, rather than the actual (moving) interface, can be considered throughout to correspond to the surface of the β phase.

To determine the relationship between the thickness of the surface layer and the solute diffusion coefficient in this layer an approach similar to that of van Liempt²¹ can be used. In homogeneous unidirectional diffusion into a semi-infinite solid:

$$\frac{c - c_i}{c_o - c_i} = \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right) \quad . \quad . \quad (7)$$

and for any $\frac{x}{2\sqrt{Dt}} > 3$, the relative concentration is of the order of 10^{-4} or less. Note that this relationship also implies that the distance d from the surface to a point of constant concentration within the solvent is proportional to $t^{\frac{1}{2}}$. Furthermore, the amount of the solute diffused into the solvent is in this case given by the parabolic law:

$$V^2 = \frac{4(c_o - c_i)^2}{\pi} Dt = kt \quad . \quad . \quad (8)$$

The above expression cannot be applied in general to diffusion-controlled reactions in which finite shapes are used as diffusion specimens. From numerical computations it is found, however, that the parabolic rate law is obeyed, to a first approximation, during the early stages of all such reactions, irrespective of the specimen shape. In particular, it can be applied to diffusion into a slab of thickness $2a$ up to the value of the parameter $Dt/a^2 = 0.16$; and into a finite cylinder of 1:5 diameter: length ratio, and radius a , for values of $Dt/a^2 \leq 0.025$. Consequently, provided the appropriate parameter value be not exceeded, both these shapes can be approximately treated as semi-infinite solids, and equation (7) can be used.

Let us first consider the diffusion into a slab of thickness $2a$. The parabolic law is in this case obeyed very closely for a considerable length of time, in fact until the relative concentration at the slab centre is

approximately 0.1. Therefore the process may be, until that time, approximately considered as that of the growth inwards, from both sides, of surface layers of minimum relative concentration limit 0.1. From the moment these two layers meet in the centre of the slab the parabolic law no longer holds. This means that the apparent solute penetration depth, i.e. the surface-layer thickness, is equal to half the thickness of the slab, a . Hence:

$$Dt/a^2 = 0.16$$

i.e.

$$a/2\sqrt{Dt} = 1.25$$

i.e.

$$d = a = 2.5\sqrt{Dt} \quad . \quad . \quad (9)$$

where d denotes the effective penetration of the diffusing solute.

This relationship between the effective penetration depth (i.e. the surface-layer thickness) and the diffusion coefficient in the layer will be assumed valid also in the case considered of heterogeneous diffusion. This assumption is thought to be justified, since at any time $t > 0$ the α/β interface may be considered as equivalent to the slab centre, in so far as the activity of the solute on either side of the interface may be assumed equal to a first approximation.

If, in the surface layer, the surface and initial concentrations are c_o^α and c_i^α , respectively, then the overall average concentration of the solute can be shown to be constant, and given by:

$$\bar{c} = c_i^\alpha + 0.452(c_o^\alpha - c_i^\alpha) \quad . \quad . \quad (10)$$

Provided now that the value of Dt/a^2 for the β phase does not exceed 0.025 for the specimens used in this work, the diffusion may be treated as unidimensional. Let us consider the following conditions:

$$\begin{aligned} D_\alpha \frac{\partial^2 c}{\partial x^2} &= \frac{\partial c}{\partial t} & D_\beta \frac{\partial^2 c}{\partial x^2} &= \frac{\partial c}{\partial t} & x, t > 0 \\ c(x, 0) &= 0 & c_\alpha(d, t) &= c_i^\alpha \\ c_\alpha(0, t) &= c_o^\alpha & d &\propto t^{\frac{1}{2}} \\ c_\beta(0, t) &= c_o^\beta & D_\beta &= \text{const.} & D_\alpha &= \text{const.} \end{aligned}$$

Then the amount of the solute absorbed by the α phase in time t is given by:

$$V_\alpha = [c_i^\alpha + 0.452(c_o^\alpha - c_i^\alpha)]d_\alpha$$

Similarly, for the β phase:

$$V_\beta = 0.452(c_o^\beta - c_i^\beta)d_\beta$$

and by (9)

$$= 1.13(c_o^\beta - c_i^\beta) \sqrt{\frac{D_\beta t}{\pi}}$$

Differentiating the above with respect to time we obtain:

$$\begin{aligned} \frac{\partial}{\partial t} (V_\alpha + V_\beta) &= \frac{1}{2t} \left\{ [c_i^\alpha + 0.452(c_o^\alpha - c_i^\alpha)] d_\alpha \right. \\ &\quad \left. + 1.13(c_o^\beta - c_i^\beta) \sqrt{\frac{D_\beta t}{\pi}} \right\} \quad . \quad . \quad (11) \end{aligned}$$

But, by Fick's law, for the overall flow across the gas/metal interface:

$$\begin{aligned} \frac{\partial V}{\partial t} &= -D_{\alpha}(c_o^{\alpha} - c_i^{\alpha}) \left. \frac{\partial c}{\partial x} \right]_{x=0} \\ &= D_{\alpha} \frac{1.412(c_o^{\alpha} - c_i^{\alpha})}{d_{\alpha}} \quad (12) \end{aligned}$$

Hence, from (11) and (12), putting $a = 0.445$ cm, and $c_i^{\beta} = 0$, as in the specimens used:

$$\begin{aligned} D_{\alpha} &= \frac{d_{\alpha}}{2.824t} \left\{ \left[\frac{c_i^{\alpha} + 0.452(c_o^{\alpha} - c_i^{\alpha})}{c_o^{\alpha} - c_i^{\alpha}} \right] d_{\alpha} \right. \\ &\quad \left. + 0.5 \frac{c_o^{\beta}}{c_o^{\alpha} - c_i^{\alpha}} \sqrt{\frac{D^{\beta}t}{a^2}} \right\} \quad (13) \end{aligned}$$

The above equation has been used to calculate the values of the diffusion coefficients of nitrogen in surface layers of α -titanium, as shown in Fig. 8.

The analysis described above is not limited to the titanium-nitrogen system, but can be applied to any other diffusion system satisfying the necessary conditions. A more rigid treatment of the same problem has been given by Wagner.²² The expression which he derives, however, is far more complex, involves the use of a parameter, and cannot be solved except by graphical methods. In view of the fact that one may expect to obtain only approximate values by such calculations, the additional approximations taken in the present analysis are thought to introduce an insignificant additional error only. Wagner's method would have to be used, however, in all cases in which the thickness of the surface layer formed is appreciable, and the assumption of the β surface remaining stationary would cause a large error.

(c) Double Surface Layer

An additional phase, γ , may be formed in the system shown in Fig. 13, provided the external gas pressure is sufficiently high. Taking again $D_{\gamma} \ll D_{\alpha}$ and making the same assumptions as in the case of a single surface layer, we obtain:

$$V_{\gamma} = [c_i^{\gamma} + 0.452(c_o^{\gamma} - c_i^{\gamma})]d_{\gamma}$$

and, differentiating

$$\begin{aligned} \frac{\partial}{\partial t} (V_{\gamma} + V_{\alpha}) &= [c_i^{\gamma} + 0.452(c_o^{\gamma} - c_i^{\gamma})] \frac{d_{\gamma}}{2t} \\ &\quad + \frac{1.412(c_o^{\alpha} - c_i^{\alpha})}{d_{\alpha}} D_{\alpha} \quad (14) \end{aligned}$$

Hence, from (12) and (14)

$$\begin{aligned} D_{\gamma} &= \frac{c_i^{\gamma} + 0.452(c_o^{\gamma} - c_i^{\gamma})}{2.824t(c_o^{\gamma} - c_i^{\gamma})} d_{\gamma}^2 \\ &\quad + \frac{c_o^{\alpha} - c_i^{\alpha}}{c_o^{\gamma} - c_i^{\gamma}} \cdot \frac{d_{\gamma}}{d_{\alpha}} \cdot D_{\alpha} \quad (15) \end{aligned}$$

The above equation has been used to calculate the values of the diffusion coefficients of nitrogen in the outer (titanium nitride) layer, shown in Fig. 9.

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REFERENCES

1. W. A. Alexander and L. M. Pidgeon, *Canad. J. Research*, 1950, [B], **28**, 60.
2. P. Ehrlich, *Z. anorg. Chem.*, 1941, **247**, 53.
3. E. A. Gulbransen and K. F. Andrew, *Trans. Amer. Inst. Min. Met. Eng.*, 1949, **185**, 741; 1950, **188**, 1063.
4. M. H. Davies and C. E. Birchenall, *ibid.*, 1951, **191**, 877.
5. J. T. Waber, G. E. Sturdy, and E. M. Wise, *U.S. Atomic Energy Commission Publ.*, 1951, (AECU-1790); also *J. Amer. Chem. Soc.*, 1953, **75**, 2269.
6. L. G. Carpenter and F. R. Reavell, *Metallurgia*, 1948, **39**, 63.
7. ———, *Watertown Arsenal Rep. No. 401/14-30*, 1952.
8. D. I. Walter, *Anal. Chem.*, 1950, **22**, 297.
9. M. W. Mallett, E. M. Baroody, H. R. Nelson, and C. A. Papp, *J. Electrochem. Soc.*, 1953, **100**, 103.
10. R. J. Wasilewski and G. L. Kehl, *Metallurgia* (in the press).
11. E. S. Bumps, H. D. Kessler, and M. Hansen, *Trans. Amer. Soc. Metals*, 1953, **45**, 1005.
12. L. C. Darken, *Symposium on Atom Movements* (Amer. Soc. Metals), 1951, 1.
13. H. J. de Boer and J. D. Fast, *Rec. Trav. Chim.*, 1936, **55**, 459.
14. O. Kubaschewski and B. E. Hopkins, "Oxidation of Metals and Alloys". 1953: London (Butterworths Scientific Publications).
15. H. Nowotny, *Planseeber. Pulvermet.*, 1953, **1**, 43.
16. A. E. Jenkins, *J. Inst. Metals*, 1953-54, **82**, (5), 213.
17. M. W. Mallett, private communication.
18. H. Ulich, C. Schwarz, and K. Cruse, *Arch. Eisenhüttenwesen*, 1936-37, **10**, 493.
19. H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids". 1947: London (Oxford University Press).
20. F. N. Rhines, *Surface Treatment of Metals* (Amer. Soc. Metals), 1941, 122.
21. J. A. M. van Liempt, *Rec. Trav. Chim.*, 1938, **57**, 871.
22. W. Jost, "Diffusion in Solids, Liquids, and Gases". 1952: New York (Academic Press).

ISOTHERMAL TRANSFORMATIONS OF EUTECTOID ALUMINIUM BRONZES *

1573

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SYNOPSIS

The eutectoid temperature for the β phase of the copper-aluminium system has been re-determined as $565^\circ \pm 2^\circ \text{C.}$, and the eutectoid composition established as $11.96 \pm 0.05\%$ aluminium. The addition of nickel to binary alloys raises the eutectoid temperature, and the eutectoid gutter rises to the four-phase plane at $605^\circ \pm 2^\circ \text{C.}$ associated with the phases α , β , γ_2 , and NiAl . The gutter moves to higher aluminium contents with increase in nickel content, and meets the edge of the four-phase plane in a triple point at about 12.7% aluminium.

A binary eutectoid alloy and similar alloys containing small amounts of nickel have been transformed isothermally in the range $350^\circ\text{--}560^\circ \text{C.}$, and the results plotted as time/temperature/transformation diagrams. Nickel has little effect on the rates of transformation, but the alloy containing 3% nickel exhibits a double knee in the curve representing the start of the eutectoid reaction. A hypothesis to explain this fact is presented.

The progress of the reactions occurring during isothermal transformations at selected temperatures was followed quantitatively in the case of the binary alloy. The results show the way in which equilibrium is approached.

The interlamellar spacing of the eutectoid formed at each transformation temperature has been determined, and a relationship found to exist between the interlamellar spacing of the eutectoid formed from the β phase and the degree of undercooling. When eutectoid is formed from the β_1 phase there is no such relationship; this is to be expected from theoretical considerations.

I.—INTRODUCTION

THE earliest isothermal transformation diagram for a eutectoid aluminium-copper alloy was published by Smith and Lindlie¹ in 1933. This work was comprehensive, and the results of subsequent investigators^{2,3} are in good agreement with it. Homogeneous β phase was obtained by annealing at 900°C. for 1 hr. before transformation. Transformations were carried out at various temperatures, from the eutectoid temperature down to 300°C. , and the results plotted in a time/temperature/transformation diagram.

The eutectoid transformation proved to be analogous to that in steels; β phase transformed to lamellar eutectoid after an induction period dependent on the temperature. The maximum rate of reaction occurred at 535°C. , although the minimum induction period was found at a lower temperature. The curves in the T/T diagram were of a simple C shape and, at higher temperatures, the interlamellar spacing decreased with falling temperature.

At 535°C. and below a new phase, β_1 ,[†] was observed, which appeared as rosette-shaped nodules within the grains and as an envelope at the grain boundaries. As the transformation temperature decreased, the speed of the $\beta \rightarrow \beta_1$ reaction apparently increased, and at 400°C. went to completion within a few seconds. The reaction seemed to influence neither the structure of the eutectoid, which grew indiscriminately through β and β_1 , nor the T/T diagram.

Pro-eutectoid α was first seen in specimens transformed at 535°C. , and large amounts formed in specimens transformed between 500° and 400°C. Since pro-eutectoid α formed only in the range of temperature in which β_1 existed, it was suggested that the eutectoid composition for β_1 lay at a higher aluminium content than that for β . It was postulated that the range of composition over which eutectoid could form from β_1 covered higher aluminium contents than was the case for β , and that the pro-eutectoid α was richer in aluminium than equilibrium α . The suggestion was made that β_1 might be the ordered body-centred cubic phase.

The M_s temperature was in the range $400^\circ\text{--}375^\circ \text{C.}$ Decomposition to eutectoid occurred below this temperature, but the observations were difficult to interpret.

Carpenter and Robertson⁴ reinterpreted the results of this investigation. They postulated that the quenched martensitic phase, β' , had a face-centred cubic lattice which was distorted by the presence of excess aluminium, and that pro-eutectoid α phase might vary from equilibrium composition to the composition of β' . They concluded that: "... below 535°C. : (1) the eutectoid change which involves diffusion becomes increasingly slower as the temperature is lowered; (2) β displays an increasing tendency to transform to α or β' as a result of a lattice change that may or may not be accompanied by diffusion."

According to them, the transformation to α "con-

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‡ Using the notation adopted in the present paper.

sists in formation of α or β' containing more aluminium than is normally soluble, and the rate of formation of this constituent at temperatures between 525° and 375° C. is more rapid than the rate of its decomposition. Consequently it is retained." This is equivalent to saying that the reaction is of a bainite type.

These authors thought that the $\beta \rightarrow \beta_1$ reaction was incidental to the main course of the reaction.

Mack² repeated the experiments on an alloy of slightly higher aluminium content. In this work, pro-eutectoid γ_2 occurred at temperatures close to the eutectoid temperature, but its amount decreased as the transformation temperature fell, and it was eventually replaced by pro-eutectoid α . Pro-eutectoid α formed at 400° C. was found to be cored after it had been held at the transformation temperature for a long time, which suggested that it was supersaturated with aluminium.

Klier and Grymko³ have reported that the interlamellar spacing of the eutectoid decreased and then increased again as the transformation temperature was lowered. They also suggested that the $\beta \rightarrow \beta_1$ transformation was a bainite-type reaction.

The investigation described in the present paper was designed to examine the reactions occurring during isothermal transformations and to determine the effect of nickel on the transformations.

II.—ALLOYS AND METHODS

Electrolytic copper, super-purity aluminium, and Mond nickel shot were used in the preparation of the alloys, whose compositions and casting temperatures are shown in Table I. The method of preparation of the alloys and their fabrication have been described previously.⁵

TABLE I.—Compositions of Experimental Alloys.

Alloy No.	Casting Temp., °C.	Copper, %	Aluminium,* %	Nickel, %	Iron, %	Silicon, %
2	1165	87.76	12.20	Nil	0.04	Trace
4	1185	86.68	12.45	0.87	Trace	Nil
6	1230	84.85	12.07	3.08	"	"
7	1250	76.09	14.88	8.40	Nil	"

* By difference.

Homogeneous β was obtained by annealing specimens, approximately $\frac{3}{16}$ in. thick, at $900^\circ \pm 10^\circ$ C. for 1 hr. before isothermal transformation in a bath of pure molten lead held within $\pm 2^\circ$ C. of the transformation temperature. Specimens transformed for very short periods were treated individually before the main group of specimens was introduced into the lead bath.⁵ Quantitative measurements were made on microsections, using a slight modification of the point-counting method described by Howard and Cohen.⁶ The method due to Mehl and his co-workers was used to measure the interlamellar spacing of the eutectoid.^{7, 8} Specimens were etched electrolytically in 1% aqueous chromic acid solution, as recommended

by Coons and Blickwede.⁹ The grains of β were approximately 1 mm. in dia.

III.—EXPERIMENTAL RESULTS

1. TEMPERATURES OF THE COPPER-ALUMINIUM EUTECTOID AND THE COPPER-ALUMINIUM-NICKEL FOUR-PHASE PLANE

From the present work the temperature of the $\beta \rightarrow \alpha + \gamma_2$ eutectoid is determined as $565^\circ \pm 2^\circ$ C., which is in good agreement with the most probable value, $565^\circ \pm 5^\circ$ C., given by Raynor¹⁰ and by Fink, Willey, and Smith.¹¹

The temperature of the four-phase plane in the copper-aluminium-nickel system, where the phases α , β , γ_2 , and NiAl coexist, is $605^\circ \pm 2^\circ$ C. The eutectoid temperature rises fairly quickly as the nickel content increases, and eutectoid began to form in

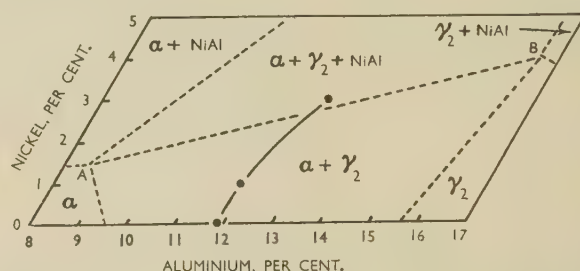


FIG. 6.—Part of the Copper-Aluminium-Nickel Diagram. The broken lines represent the phase boundaries at 500° C. according to Alexander.¹² The solid line represents the eutectoid gutter, which rises from the binary eutectoid to the four-phase plane at 605° C.

Alloy 4 (0.87% nickel) at $582^\circ \pm 2^\circ$ C. and in Alloy 6 (3.08% nickel) at $605^\circ \pm 2^\circ$ C. The composition of Alloy 6 lies close to the tie-line between the α and γ_2 phases, AB in Fig. 6,¹² and is on the nickel-poor side of the tie-line, since no NiAl has been detected in specimens of Alloy 6, irrespective of the heat-treatment.

2. ISOTHERMAL TRANSFORMATIONS OF ALLOYS 2, 4, AND 6

The β phases in these alloys undergo martensite transformations in the range 350°–400° C., and the present paper is limited to a consideration of the reactions that occur above these temperatures.

The courses of isothermal transformations in similar alloys have been described in detail by Smith and Lindlie¹ and by Mack,² and a detailed account is not now given. However, the courses of such reactions follow a general pattern: first, there is an induction period in which no change can be observed in the microstructure; particles of pro-eutectoid phase then appear and grow. Later, nodules of eutectoid are observed, and these develop into the high-temperature phase until the specimen is transformed completely

into eutectoid plus pro-eutectoid phase. During the later stages of a transformation, the eutectoid and pro-eutectoid phases may grow simultaneously. In all cases eutectoid is nucleated mainly at grain boundaries.

At lower transformation temperatures a change occurs in the β phase, which is superimposed on the above pattern. In the present paper, the change is

is in excellent agreement with those determined by earlier investigators.¹⁻³

Several interesting features have been observed, and these are noted below.

(i) During the $\beta \rightarrow \beta_1$ transformation, β_1 forms as an envelope at the grain boundaries of β and as numerous nodules or rosettes within the grains. The appearance of the $\beta + \beta_1$ structure is illustrated in

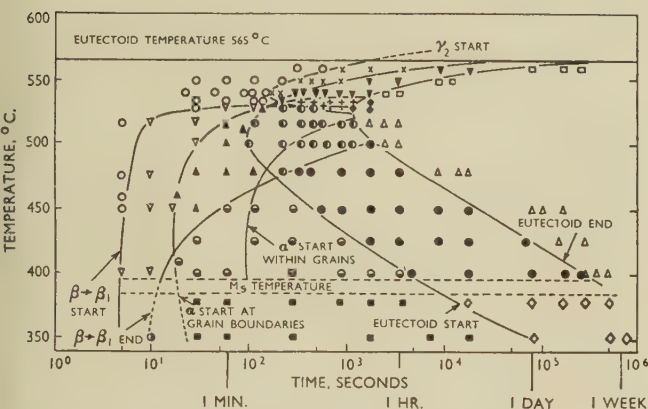


Fig. 7.—Time/Temperature/Transformation Diagram for Alloy 2.

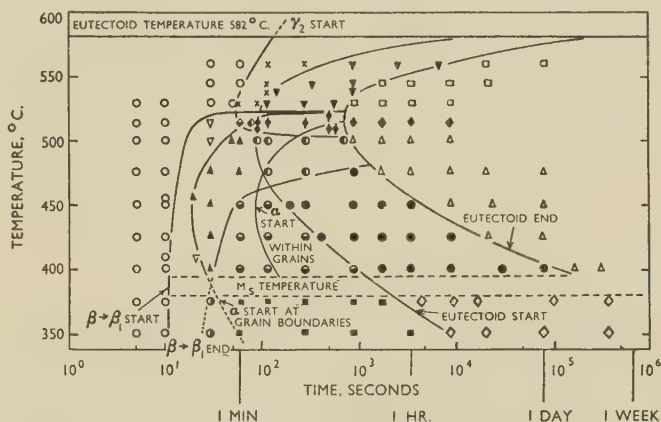


Fig. 8.—Time/Temperature/Transformation Diagram for Alloy 4.

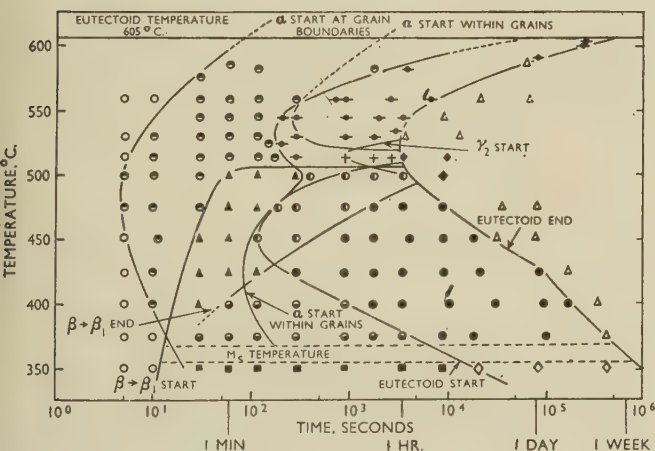


Fig. 9.—Time/Temperature/Transformation Diagram for Alloy 6.

KEY TO FIGS. 7-9.

- | | |
|---|--|
| ○ β | ▲ $\alpha + \beta + \beta_1$ |
| ● $\alpha + \beta$ | ◆ $\beta + \beta_1 + \gamma_2$ |
| × $\beta + \gamma_2$ | ◊ $\alpha + \beta + \beta_1 + \gamma_2$ |
| △ $\alpha + \text{eutectoid.}$ | ⊙ $\alpha + \beta + \beta_1 + \text{eutectoid}$ |
| □ $\gamma_2 + \text{" "}$ | ⊖ $\alpha + \beta + \beta_1 + \gamma_2 + \text{eutectoid}^*$ |
| ◇ $\alpha + \gamma_2 + \text{eutectoid}$ | ⊗ $\alpha + \beta_1$ |
| ⊕ $\alpha + \beta + \text{" "}$ | ● $\alpha + \beta_1 + \text{eutectoid}$ |
| ▽ $\beta + \gamma_2 + \text{" "}$ | ⊙ $\beta_1 + \beta'$ |
| + $\alpha + \beta + \gamma_2 + \text{eutectoid.}$ | ■ $\alpha + \beta_1 + \beta'$ |
| ▽ $\beta + \beta_1$ | ◇ $\alpha + \beta_1 + \beta' + \text{eutectoid}$ |

* The symbol on the left has been used in Fig. 7 to enable a curve to be drawn.

called the $\beta \rightarrow \beta_1$ transformation, since it is thought that β_1 is the ordered form of β . The change begins before the separation of pro-eutectoid constituents and occurs fairly quickly. At temperatures immediately below that at which β_1 first appears, equilibrium is set up between β and β_1 , and both phases persist until the eutectoid reaction is complete.

The time/temperature/transformation diagrams are shown in Figs. 7-9. In Alloys 2 and 4 the knees of the "start" and "end" curves for the eutectoid reaction are displaced with respect to temperature, and Alloy 6 exhibits two knees in the "start" curve and only one in the "end" curve. The $T/T/T$ curve for Alloy 2

Fig. 2 (Plate XX). With passage of time the envelope of β_1 thickens and the nodules grow and become larger and less numerous; β phase etches more darkly than β_1 . The transformation is not detected in this form in Alloy 6, and a duplex structure is not shown. At lower temperatures, in partially transformed specimens of Alloy 6, β appears uniformly dark brown when examined at low magnifications. At very high magnification the structure is minutely cellular and similar to structures associated with the ordering of certain iron-nickel-aluminium alloys reported by Bradley.^{13, 14} It is assumed that dark-etching of β indicates that the $\beta \rightarrow \beta_1$ transformation is in progress. On this assumption the curves

relating to the start and finish of the reaction have been drawn. The curves are of the same shape as those for Alloys 2 and 4.

(ii) In the range of temperatures in which β and β_1 coexist during the formation of eutectoid, the eutectoid shows pseudomorphs of the $\beta + \beta_1$ structure (Fig. 1, Plate XX).

amount of α greatly increases. At 515° and 500° C. small amounts of pro-eutectoid γ_2 also form.

(iv) Pro-eutectoid α occurs as a grain-boundary precipitate and as long thin needles (not plates¹⁵). Grain-boundary α appears first, and is the only form in specimens in which the amount of α is small. Curves are drawn in the $T/T/T$ diagrams represent-

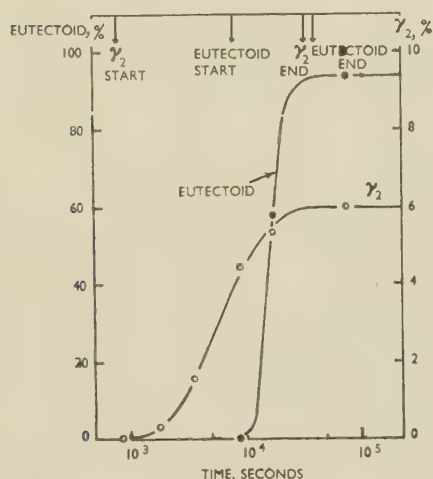


FIG. 10.—Transformed at 560° C.

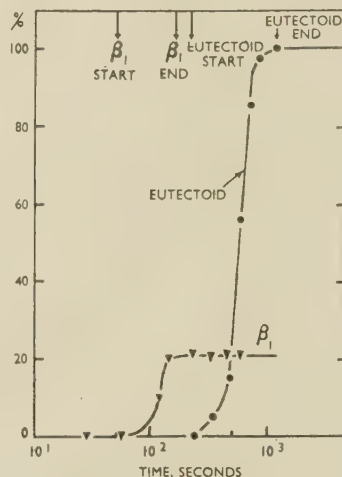


FIG. 11.—Transformed at 527° C.

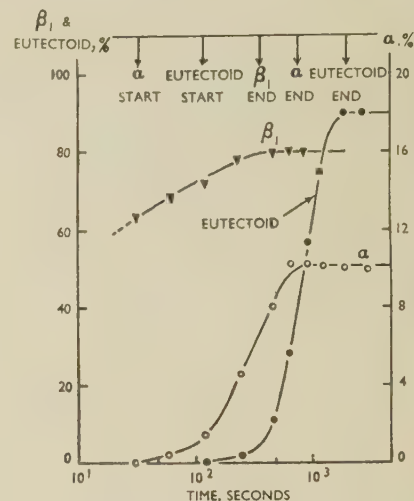


FIG. 12.—Transformed at 500° C.

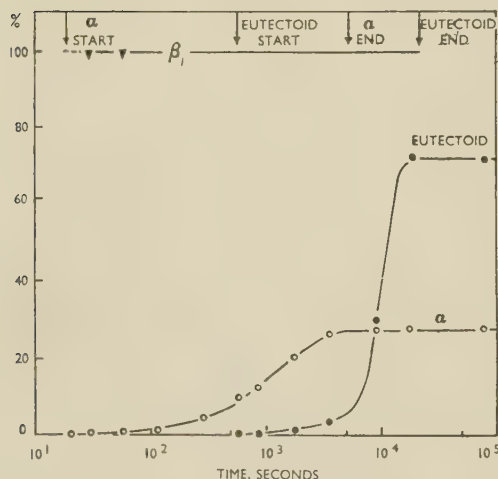


FIG. 13.—Transformed at 450° C.

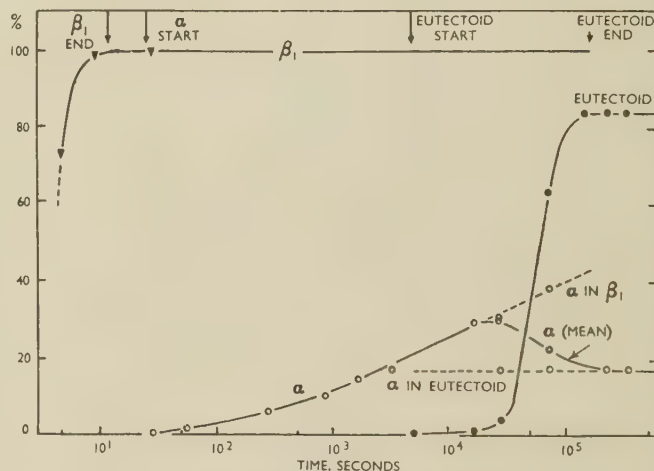


FIG. 14.—Transformed at 400° C.

FIGS. 10-14.—Percentage-Constituent/Time Diagrams for Alloy 2.

(iii) In Alloys 2 and 4, at transformation temperatures near to the eutectoid temperature, the pro-eutectoid constituent is γ_2 and at lower temperatures is α . A narrow range of temperatures exists in which both pro-eutectoid α and γ_2 occur.

In Alloy 6 the pro-eutectoid constituent is α in all cases. At high transformation temperatures considerable amounts of α form, and the amount decreases to a minimum at 515° C., when less than 0.5% is found. At lower transformation temperatures the

ing the start of precipitation of both forms. Pro-eutectoid γ_2 does not form preferentially at the grain boundaries.

(v) Pro-eutectoid α , which forms from a matrix of $\beta + \beta_1$, is always surrounded by a sheath of β_1 , but pro-eutectoid γ_2 is not surrounded by such a sheath (Fig. 3, Plate XX).

(vi) In specimens of Alloys 2 and 4 transformed for long periods at 400° C. pro-eutectoid α shows coring (Fig. 4, Plate XX).

(vii) Pro-eutectoid α formed in specimens of Alloy 6 is dark-etching and feathery in appearance, similar to that formed during the quenching of 60:40 brass from high temperatures.

3. TRANSFORMATION/TIME CURVES

The percentage transformation/time curves at selected temperatures for the phases and constituents in Alloy 2 are shown in Figs. 10–14. The start and end of the reactions are indicated by vertical arrows above the curves. The curves are of the form expected for reactions which proceed by nucleation and growth. In the absence of data concerning the nucleation of the phases and constituents, the kinetics of the reactions cannot be discussed. However, from a consideration of the relative positions of the curves with respect to time, it is concluded that, in the range of transformation temperatures from 560° to 450° C.,

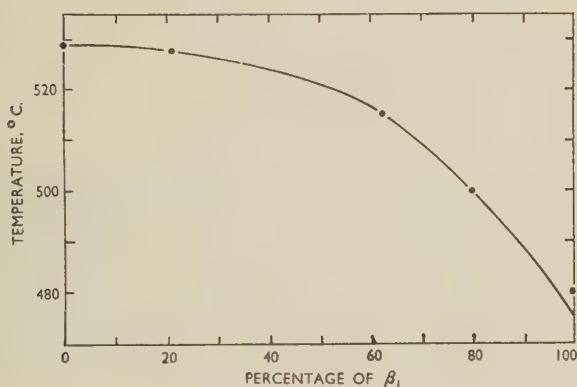


Fig. 15.—Percentage β_1 in Equilibrium with β /Temperature Diagram for Alloy 2.

precipitation of the amount of pro-eutectoid constituent in equilibrium with β (or β_1) is practically complete before a large amount of eutectoid has formed. Below 450° C. precipitation of pro-eutectoid constituent and that of eutectoid occur simultaneously, and the amount of pro-eutectoid constituent does not reach the equilibrium value.

In the transformation at 400° C. the amount of pro-eutectoid α present in the specimens reaches a maximum value at an intermediate time and then decreases. The amount of α in regions of untransformed β_1 increases with time and the amount of α in the eutectoid matrix is sensibly constant, irrespective of time of transformation. This suggests that pro-eutectoid α is partially absorbed by eutectoid. Pro-eutectoid α is supersaturated with aluminium, with respect to α in eutectoid, and supersaturation is gradually relieved by precipitation of γ_2 on γ_2 lamellae in adjacent eutectoid. This will account for the cored appearance of pro-eutectoid α in specimens held at the transformation temperature for long periods (Fig. 4, Plate XX).

The curves for the β_1 phase for 527° and 500° C. (Figs. 11 and 12) indicate that equilibrium between β and β_1 is quickly set up and that the lower the transformation temperature the greater the amount of β_1 present under equilibrium conditions. A curve relating percentage β_1 in equilibrium with β is shown in Fig. 15. The point for 480° C. does not lie on any smooth curve which can be drawn through the other points, and this is attributed to the formation of large amounts of pro-eutectoid α phase (see the discussion of results in Section IV). Previously,^{1,2} the persistence in the microstructure of the cellular appearance associated with the $\beta \rightarrow \beta_1$ transformation had been interpreted as showing that this $\beta \rightarrow \beta_1$ reaction was slower than the eutectoid reaction, but the above data show this to be untenable.

4. CHANGE IN EUTECTOID COMPOSITION WITH TRANSFORMATION TEMPERATURE

Curves relating the amounts of pro-eutectoid constituents present in completely transformed specimens to transformation temperature are reproduced in Figs. 16–18. The curves (Figs. 10–13) for Alloy 2 showed that the amounts of pro-eutectoid constituent present in completely transformed specimens is the amount which is in equilibrium with β or β_1 before its transformation to eutectoid. Thus, Figs. 16–18 may be regarded as a measure of the change of eutectoid composition with transformation temperature.

In Alloys 2 and 4 pro-eutectoid γ_2 exists at high temperatures and α at lower temperatures, and γ_2 ceases to form and α begins to form in the temperature ranges 527°–534° C. and 510°–515° C., respectively. In Alloy 6 the pro-eutectoid constituent at all temperatures is α , but at 515° and 500° C. the amount of α is slight and small quantities of pro-eutectoid γ_2 also form. The critical temperatures for β_1 formation are, respectively, 529°, 524°, and 500°–515° C. for Alloys 2, 4, and 6. Thus, the temperatures at which pro-eutectoid γ_2 formation ceases and pro-eutectoid α formation begins are close to the temperatures at which the $\beta \rightarrow \beta_1$ transformation sets in. It is believed that there is no significance in the coincidence of these temperatures and that changes in pro-eutectoid constituent are due not to β_1 formation but to the form of the metastable equilibrium diagram which exists below the eutectoid temperature (see Section IV). However, the β_1 phase will influence the amount of pro-eutectoid α formed at lower temperatures and may be responsible for the sharp inflection in the curve (Fig. 18) at about 500° C.

5. INTERLAMELLAR SPACING

The interlamellar spacing of eutectoid in a binary eutectoid alloy has been reported first to decrease and then to increase again as the transformation temperature is lowered.³ Quantitative measurements on the present alloys (Fig. 19) confirm this.

In the case of pearlite in steel, Zener¹⁶ and, more recently, Fisher¹⁷ have shown theoretically that a relationship should exist between the minimum possible interlamellar spacing and the degree of undercooling. The minimum possible interlamellar spacing is that resulting when all the free energy liberated by the reaction is used to form interfaces between the two phases which comprise the lamellæ. Zener showed that the fastest rate of growth occurred when the interlamellar spacing was twice the minimum possible value, and this is the most probable interlamellar

predicted. At lower temperatures eutectoid will form from a mixture of β and β_1 or from β_1 alone, and a deviation from the straight-line relationship is to be expected. An increase in interlamellar spacing is also expected since the free energy available for the formation of interfaces will be less. This is because free energy is liberated in forming β_1 and the free energy released in passing from one state to another is independent of the "path" of the reaction. Formation of β_1 will have its effect at all transformation temperatures below that at which the $\beta \rightarrow \beta_1$

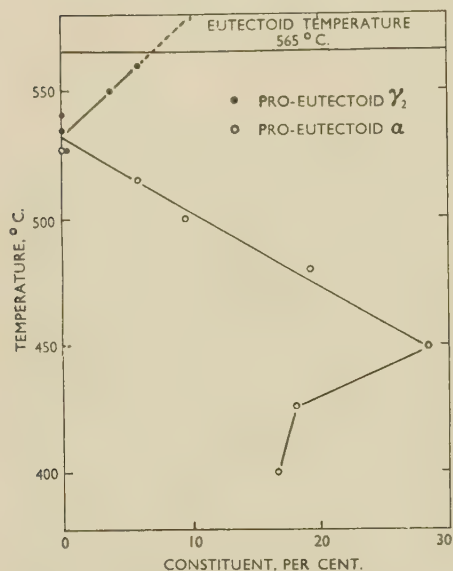


FIG. 16.—Percentage Pro-Eutectoid Constituent/Temperature Diagram for Alloy 2.

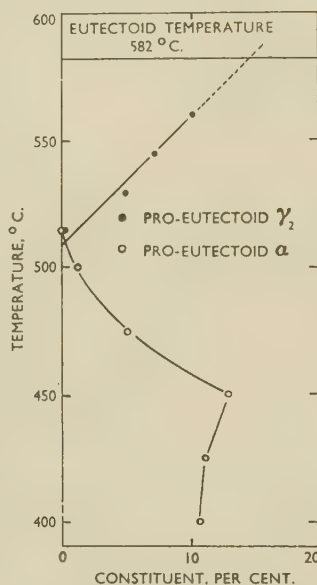


FIG. 17.—Percentage Pro-Eutectoid Constituent/Temperature Diagram for Alloy 4.

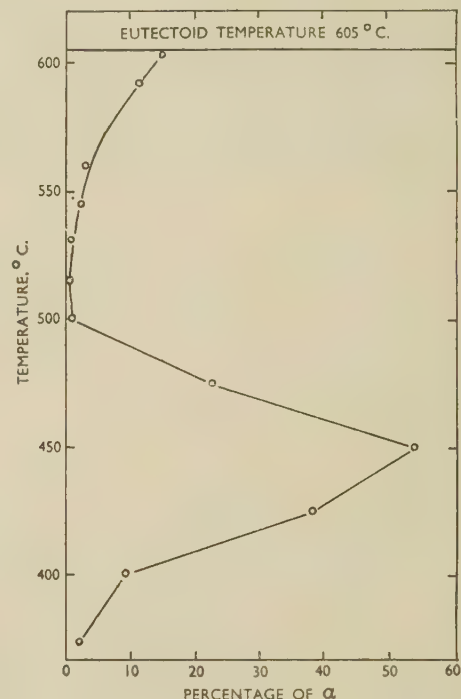


FIG. 18.—Percentage Pro-Eutectoid Constituent/Temperature Diagram for Alloy 6.

spacing to be formed. The equation relating the most probable spacing to the degree of undercooling, $(T_e - T)$, is:

$$S_0 = 4ST_e/(T_e - T)Qr$$

where S_0 = the most probable interlamellar spacing, S = the interfacial energy per unit area, Q = the heat of transformation per unit mass, r = the specific gravity, T_e = the eutectoid temperature, T = the transformation temperature.

If Zener's hypothesis is correct, the experimental results when plotted using logarithmic scales will lie on a line of slope -1 . This is true in the case of pearlite in steels.⁸

The hypothesis may be applied to the aluminium bronzes, but in this case an added complication is present. At high temperatures the eutectoid forms from β and at lower temperatures from β_1 . When eutectoid forms from β the relationship between interlamellar spacing and degree of undercooling will be as

reaction is first observed. In the range of temperatures where eutectoid forms from β_1 , the relationship between interlamellar spacing and degree of undercooling cannot be predicted.

Regression lines have been fitted to the points associated with eutectoid formed from β phase in Fig. 19, and in all cases the slopes of the lines are close to -1 , as indicated below:

Alloy 2	-1.05
Alloy 4	-1.15
Alloy 6	-1.08

It is concluded that, within the limits of experimental error, the relationship predicted by theory holds above the temperature at which β_1 is first observed, and that the $\beta \rightarrow \beta_1$ transformation has an important effect on the eutectoid that is not indicated on the $T/T/T$ diagram.

Eutectoid formed from regions of the duplex structure, $\beta + \beta_1$, shows pseudomorphs of the struc-

ture, Fig. 1 (Plate XX). This is possibly due to slight variations in interlamellar spacing between eutectoid formed from β and β_1 , since the spacing will be greater in β_1 regions than in β regions.

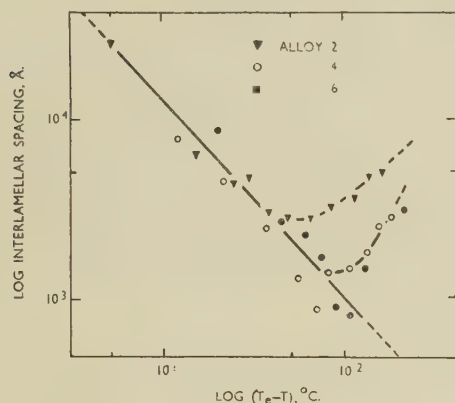


FIG. 19.—Interlamellar Spacing/Degree of Undercooling Diagram for Alloys 2, 4, and 6.

6. HARDNESS OF COMPLETELY TRANSFORMED SPECIMENS

Curves relating micro- and macro-hardness to transformation temperature are shown, respectively, in Figs. 20 and 21. In both cases hardness values were measured by means of diamond pyramid indenters.

The microhardness curves (Fig. 20) show that the hardness of the eutectoid reaches a maximum in the range 530°–500° C. and then decreases. The temperatures at which the maximum hardness values are found correlate well with those at which the

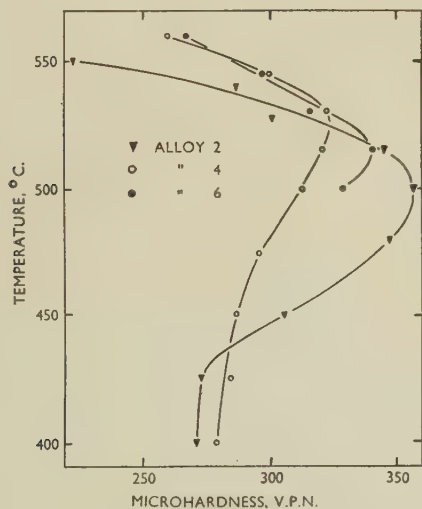


FIG. 20.—Microhardness/Temperature Curves.

minimum interlamellar spacings occur. The curve for Alloy 6 is not plotted for temperatures lower than 500° C., because very large amounts of pro-eutectoid α are formed at these temperatures.

The initial sharp rises with increase in degree of undercooling in the curves of Fig. 21 are attributed to a decrease in the interlamellar spacing of the eutectoid, but the amounts of pro-eutectoid constituents also decrease. The fall in hardness at lower transformation temperatures has been attributed to the presence of increasing quantities of pro-eutectoid α ,¹ but the increase in interlamellar spacing also contributes to the decrease in hardness, cf. the micro-hardness curves (Fig. 20). The minimum that occurs in each curve is associated with the presence of a maximum amount of pro-eutectoid α , cf. Figs. 16–18 and Fig. 21. The increase in hardness at low temperatures is due to the smaller amount of pro-eutectoid α which remains in completely transformed specimens, and the

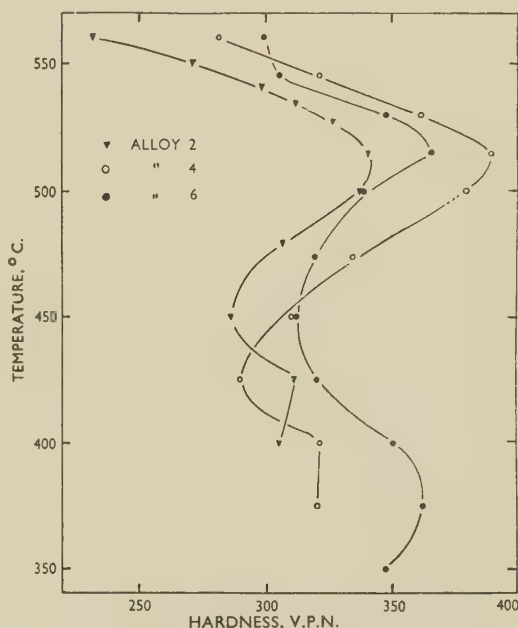


FIG. 21.—Hardness/Temperature Curves.

hardness rises despite the fact that the interlamellar spacing continues to increase.

IV.—DISCUSSION OF RESULTS

1. THE $\beta \rightarrow \beta_1$ TRANSFORMATION

Below the eutectoid temperature, β and β_1 are metastable phases, and the relationship between them can be considered without reference to the stable phases. In the absence of nuclei of the stable phases equilibrium can be set up between the metastable phases, and this condition appertains in the early stages of the isothermal transformations.

In the binary system the relationship between β and β_1 can be represented by an equilibrium diagram in which two single-phase regions are separated by a two-phase region. β exists at high and β_1 at low temperatures, and when the two phases are in equilibrium with each other β_1 is richer in aluminium than β .

For a given composition the two phases can coexist over a limited range of temperature, and in the case of Alloy 2 this range is roughly from 529° to about 480° C. Precipitation of pro-eutectoid α is accompanied by rejection of aluminium to the $\beta + \beta_1$ matrix, which becomes enriched in aluminium adjacent to the α , and a sheath of β_1 forms around the α . This implies that β_1 is aluminium-rich and β copper-rich. The suggestion that, in similar alloys, pro-eutectoid α will form only from β_1 is not tenable.

At 480° C. β transforms completely to β_1 , but in Fig. 15 the point corresponding to 480° C. and 100% β_1 does not lie on any smooth curve that can be drawn through the other points. About 20% of the specimen transforms to pro-eutectoid α at this temperature, and the matrix is sufficiently enriched in aluminium to allow the whole of the matrix to transform to β_1 .

Consideration of various data enables an idea to be gained of the nature of β_1 . The alloys are close to the composition Cu_3Al , e.g. Alloy 2 contains 24.6 at.-% aluminium. When β phase of approximately eutectoid composition is quenched, an ordered martensitic phase is always obtained.^{18, 19} An alloy with 14.7% aluminium does not transform to martensite above room temperature, and the lattice structure obtained on cooling to room temperature is ordered body-centred cubic.²⁰ It is unlikely that ordering will occur in the eutectoid alloy after the martensitic phase has formed. The M_s temperature for the eutectoid alloys is about 380° C., and it is reasonable to look for the ordering reaction at higher temperatures. Above the eutectoid temperature the β phase is disordered,^{19, 21} and the ordering reaction must occur below the eutectoid temperature, 565° C. Thus, the ordering reaction probably occurs in the range of temperatures examined in the present work.

The transformation from β to β_1 occurs by nucleation and growth. The number of nuclei formed is large and there is little preferential nucleation at the grain boundaries. The nuclei grow as rosette-shaped nodules, whereas most precipitates formed in the solid state take up a preferred orientation with respect to the lattice of the parent phase, usually assuming a characteristic shape, e.g. α phase in these alloys usually takes the form of needles.¹⁵ The interfacial energy between β and β_1 is probably small, and the very efficient nucleation within the grains suggests that the lattices of the phases are similar.

Some etching reagents show up the duplex $\beta + \beta_1$ structure and others the structure of the martensitic phase formed on quenching. The martensitic needles run indiscriminately through areas of β and β_1 and stop only at grain boundaries of the original β phase, or when they meet other martensitic needles. Thus, within a single grain the orientations of β and β_1 regions are apparently the same. It is significant that all the nodules of β_1 within a single β grain apparently have the same orientation. In general, when a second phase separates from a solid solution there are several possible orientations, relative to the parent lattice, which it may take. It is probable that the

difference between β and β_1 is one not of lattice but of arrangement of atoms within the lattice, i.e. ordering.

All the observations recorded are consistent with the hypothesis that the $\beta \rightarrow \beta_1$ transformation is an ordering reaction.

2. THE BEHAVIOUR OF THE PRO-EUTECTOID CONSTITUENTS IN THE BINARY ALLOY

The percentage transformation/time curves (Figs. 10–13) show that, at temperatures above 450° C., equilibrium is set up between the pro-eutectoid phase and β or β_1 , before a large amount of eutectoid has formed. The amount of pro-eutectoid constituent formed at each transformation temperature enables a qualitative picture of the equilibrium diagram between

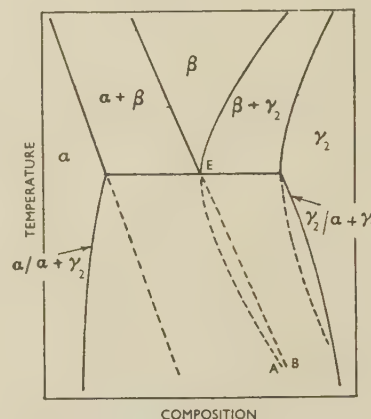


FIG. 22.—Hypothetical Phase Diagram for α , β , and γ_2 Phases.

pro-eutectoid phase and β or β_1 to be drawn for temperatures below the eutectoid temperature.

The alloy is slightly hyper-eutectoid at the eutectoid temperature, and as the transformation temperature is lowered the amount of pro-eutectoid γ_2 formed becomes smaller and eventually none forms. This implies that below the eutectoid temperature the $\beta(\beta + \gamma_2)$ phase boundary moves to higher aluminium contents, as is shown qualitatively in Fig. 22. This is analogous to the behaviour of the $\beta/(\beta + \gamma)$ phase boundary in the copper–zinc system.

The maximum amount of pro-eutectoid γ_2 observed forms at the highest transformation temperature, close to the eutectoid temperature. Possibly, greater amounts of γ_2 may form above the eutectoid temperature. β in equilibrium with γ_2 reaches a composition of minimum aluminium content at or above the eutectoid temperature. In the latter case the stable equilibrium diagram will have analogy with the copper–silicon diagram, in which the $\kappa(\alpha + \kappa)$ phase boundary moves to lower silicon contents as the temperature decreases.

At temperatures in the range 529°–450° C. the pro-eutectoid phase is α and the “parent” phases $\beta + \beta_1$ or β_1 . The phase relationships in the range of temperature in which β transforms to β_1 are compli-

cated, but it is concluded that the main effect of the change on the phase relationships is to alter the gradients of the phase boundaries in the "equilibrium" diagram. Progressively larger amounts of pro-eutectoid α are formed as the transformation temperature is lowered, implying that the $\alpha + \beta_1$ phase region in the "equilibrium" diagram moves to higher aluminium contents as the temperature falls. The relationships are shown, qualitatively, in Fig. 23, and in the absence of eutectoid the phase boundaries postulated do exist.

The compositions of the phases in the eutectoid are independent of the phase or phases from which the eutectoid forms, and the phase boundaries of the $\alpha + \gamma_2$ regions are not affected by the formation of β_1 .

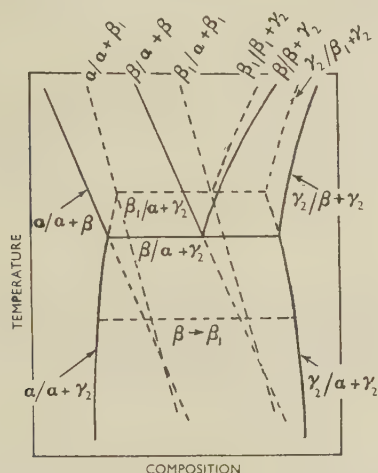


FIG. 23.—Hypothetical Phase Diagram for α , β , and β_1 Phases.

Pro-eutectoid phase formed before the eutectoid has a composition different from that of the same phase in the eutectoid. When β or β_1 has transformed to eutectoid the pro-eutectoid constituent will readjust its composition to that of the same phase in the eutectoid, if held for a sufficiently long time at temperature. This is a slow diffusion process and will lead to chemical heterogeneity in the pro-eutectoid constituent, which may exhibit coring. The lamellae of eutectoid may also grow into the pro-eutectoid constituent, and a microsection taken close to a particle of constituent may show a discontinuity in the structure of the eutectoid (Fig. 5, Plate XX).

In the temperature range 525°–540° C. both pro-eutectoid constituents are formed in small amounts. This suggests that the composition of the alloy lies within a field such as *EAB* in Fig. 22, and that *EA* and *EB* are close together.

3. THE EFFECT OF NICKEL

(a) The Formation of the Double Knee in the T/T Diagram

It is postulated that separate *C* curves can be drawn for the decomposition of β and β_1 into eutectoid.

Above the temperature at which β_1 is first observed the experimentally determined *C* curve is that for the β phase, and below the temperature at which β is last observed the experimentally determined *C* curve is that for the β_1 phase. In the intermediate range of temperature, in which β and β_1 can coexist in "equilibrium", the decomposition of both β and β_1 will contribute to the experimental curve.

If the knees of the two curves are fairly close together, no discontinuity will be observed in the experimental curve, although some of the properties of the final product may show anomalous variations with respect to temperature of formation. When the curves are separated to a greater extent, the knee of the experimental curve will become deeper, and eventually a double knee will appear in the experimental curve. The separation of the knees in the "start" curves and not in the "end" curves for the eutectoid reaction is due to plotting time on a logarithmic scale.

It is suggested that the addition of nickel to binary copper-aluminium alloys either depresses the knee of the curve for β_1 or raises the knee of the curve for β , or both.

(b) Interlamellar Spacing

The form of the interlamellar-spacing curves (Fig. 19) is the same in all cases. In the temperature range in which the eutectoid forms from β the interlamellar spacing is a function of the degree of undercooling, and within the limits of experimental error the lines superimpose when plotted on logarithmic scales. Nickel has no effect on the interlamellar spacing of the eutectoid.

(c) The Rates of Reaction

Nickel has little effect on the induction periods for the eutectoid reaction or on the rates of reaction. It slightly increases the number of nuclei from which nodules of eutectoid grow, but the number of nuclei is small in all cases, and nucleation occurs mainly at grain boundaries.

The physical properties of nickel are very similar to those of copper, and its atomic diameter differs from that of copper by only a few per cent. Guillet²² showed that it behaved in a manner analogous to copper when it replaced the latter in alloys of copper with zinc, tin, or aluminium. Thus the behaviour of nickel is not unexpected.

(d) The $\beta \rightarrow \beta_1$ Reaction

In the alloys studied, the nickel lowered the temperature at which β_1 phase was first observed. In the alloy containing 3% nickel, the reaction was accompanied by a general darkening of the β phase, and not by formation of the nodular structure.

(e) The Martensite Reaction

The M_s temperatures of the nickel-bearing alloys are lower than that of the binary alloy. (The M_s temperatures reported refer to the β_1 phase.)

(f) *The Eutectoid Composition*

The composition of the eutectoid at the eutectoid temperature has been estimated from the data in Figs. 16-18, and the results of previous investigators.^{10, 12, 23} No correction has been made for the error arising from the difference between weight and volume percentages. The addition of 3% nickel causes the eutectoid composition to move to slightly higher aluminium contents (Fig. 6) and the eutectoid gutter meets the edge of the four-phase plane, at 605° C., and about 12.7% aluminium.

Using specific-gravity values for β and γ_2 phases, estimated by D. L. Thomas, to calculate weight percentages of constituents, the binary eutectoid composition is $11.96 \pm 0.05\%$ aluminium.

(g) *The Pro-Eutectoid Constituents*

The behaviour of the nickel-bearing alloys is similar to that of the binary alloy, as indicated by Figs. 16-18. The behaviour of Alloy 4, which contains pro-eutectoid γ_2 at the eutectoid temperature, is qualitatively the same as that of Alloy 2, and in-

dicates that below the eutectoid temperature the $\beta/(\beta + \gamma_2)$ phase boundary in the "equilibrium" diagram moves towards higher aluminium contents as the temperature is lowered. Alloy 6 contains pro-eutectoid α at the eutectoid temperature, and as the transformation temperature is lowered the amount formed before eutectoid formation decreases. This suggests that the $(\alpha + \beta)/\beta$ phase boundary moves towards lower aluminium contents as the temperature decreases. The formation of β_1 appears to reverse this trend.

ACKNOWLEDGEMENTS

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REFERENCES

1. C. S. Smith and W. E. Lindlief, *Trans. Amer. Inst. Min. Met. Eng.*, 1933, **104**, 69.
2. D. J. Mack, *ibid.*, 1947, **175**, 240.
3. E. P. Klier and S. M. Grymko, *ibid.*, 1949, **185**, 611.
4. H. C. H. Carpenter and J. M. Robertson, "Metals", Vol. 2, pp. 1282-1285. 1939: Oxford (University Press).
5. R. Haynes, *J. Inst. Metals*, 1953-54, **82**, 493.
6. R. T. Howard and M. Cohen, *Trans. Amer. Inst. Min. Met. Eng.*, 1947, **172**, 413.
7. M. Gensamer, E. B. Pearsal, W. S. Pellini, and J. R. Low, Jr., *Trans. Amer. Soc. Metals*, 1942, **30**, 983.
8. G. E. Pellissier, M. F. Hawkes, W. A. Johnson, and R. F. Mehl, *ibid.*, 1942, **30**, 1049.
9. W. C. Coons and D. J. Blickwede, *ibid.*, 1945, **35**, 284.
10. G. V. Raynor, *Inst. Metals Annotated Equilib. Diagr. Series*, No. 4, 1944.
11. W. L. Fink, L. A. Willey, and C. S. Smith, *Metals Handbook (Amer. Soc. Metals)*, 1948, p. 1159.
12. W. O. Alexander, *J. Inst. Metals*, 1938, **63**, 163.
13. A. J. Bradley, *J. Iron Steel Inst.*, 1951, **168**, 233.
14. A. J. Bradley, *ibid.*, 1952, **171**, 41.
15. R. F. Mehl and O. T. Marzke, *Trans. Amer. Inst. Min. Met. Eng., Inst. Metals Div.*, 1931, 123.
16. C. Zener, *Trans. Amer. Inst. Min. Met. Eng.*, 1946, **167**, 550.
17. J. C. Fisher, *Symposium on Thermodynamics and Physical Metallurgy (Amer. Soc. Metals)*, 1950, p. 201.
18. A. B. Greninger, *Trans. Amer. Inst. Min. Met. Eng.*, 1939, **133**, 204.
19. G. Wassermann, *Metallwirtschaft*, 1934, **13**, 133.
20. V. Gawranek, E. Kaminsky, and G. Kurdjumow, *ibid.*, 1936, **15**, 370.
21. E. Kaminsky, G. Kurdjumow, and W. Neumarx, *ibid.*, 1934, **13**, 373.
22. L. Guillet, *Rev. Mét.*, 1923, **20**, 130.
23. A. J. Bradley and H. Lipson, *Proc. Roy. Soc.*, 1938, [A], **167**, 421.

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SYNOPSIS

Strain-ageing has been observed during tensile tests on 70:30 brass strip. The results are interpreted in terms of Cottrell's theory (*Phil. Mag.*, 1953, [vii], 44, 829).

THE phenomena of the discontinuous yield point and of strain-ageing, which are so well known in mild steel, are not usually believed to appear in polycrystalline

11-15), the yield point was either reduced in magnitude or completely eliminated.

It can be seen from Fig. 1 that the stress/strain curve becomes stepped after the specimen has been strained appreciably (~7%). Cottrell⁴ has examined the same phenomenon of the stepped stress/strain curve in aluminium alloys and has amplified the idea that it is due to the solute atoms diffusing through the lattice at a speed sufficient to allow strain-ageing while plastic deformation is in progress. The measured rate of diffusion of the solute atoms in annealed aluminium at room temperature is not high enough to give simultaneous ageing and yielding, and Cottrell suggests that the rate of diffusion is accelerated appreciably by the formation of lattice vacancies during the plastic deformation. The number of vacancies, and hence the rate of diffusion, increases with the amount of plastic strain, so that the serrations or steps in the stress/strain curve should appear only after a certain amount of strain, and they should also increase in magnitude as the strain is increased. Fig.

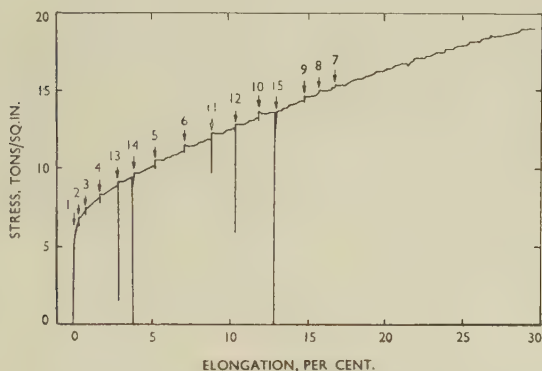


FIG. 1.—Tensile Stress/Strain Curve of 70:30 Brass Strip, Showing the Yield Points Produced by Ageing at Room Temperature. Strain rate = 0.0003 sec.⁻¹. Temp. = 21° C.

KEY.

- | | | | |
|------|---------------|---|-----------------------------|
| 1-6. | Rested 1 min. | | |
| 7. | " 5 sec. | | |
| 8. | " 10 sec. | | |
| 9. | " 20 sec. | | |
| 10. | " 2 min. | | |
| 11. | " 1 min. | Load dropped to 9 tons/in. ² . | |
| 12. | " 2 min. | " " | 6 " |
| 13. | " 3½ min. | " " | 1½ " |
| 14. | " 4 min. | " " | 0 " |
| 15. | " 5 min. | " " | " and extensometer removed. |

brass, although occasional references to their occurrence have been made.¹⁻³ During some tensile tests, using an autographic extensometer, on 70:30 brass strip, however, strain-ageing was definitely found to occur, although no initial yield point could be detected. The specimens were strained slightly and were allowed to age under load for about 1 min.; a small yield point then appeared on continuation of the test (Fig. 1). It was found that the size of the yield point (after one minute's ageing) increased as the amount of strain was increased (points 1-6 in Fig. 1), and at high strains it was found that a detectable yield point appeared after only 5 seconds' ageing (point 7). The yield points which are obtained after ageing are apparently affected by slight stress concentrations, by misalignment of the specimen, or by the large hysteresis loop shown by the brass. When the load was allowed to drop appreciably during ageing (points

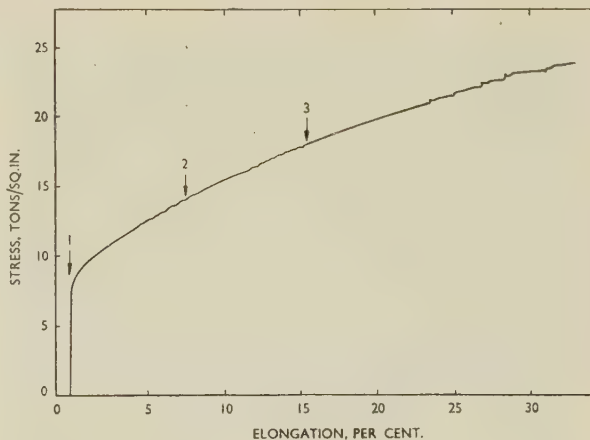


FIG. 2.—The Effect of the Speed of Testing on the Stepped Stress/Strain Curve of 70:30 Brass. Temp. = 21° C.

KEY.

- | | |
|----|--|
| 1. | Strain rate = 0.00018 sec. ⁻¹ |
| 2. | " " increased to 0.0018 sec. ⁻¹ |
| 3. | " " " 0.0061 sec. ⁻¹ |

1 indicates that brass behaves in this manner, and it is probable that the repeated yielding observed here can be explained by Cottrell's hypothesis. If this

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idea is correct, the strain at which the steps first appear should be dependent on the rate of testing. If the strain rate is increased, the rate of diffusion of

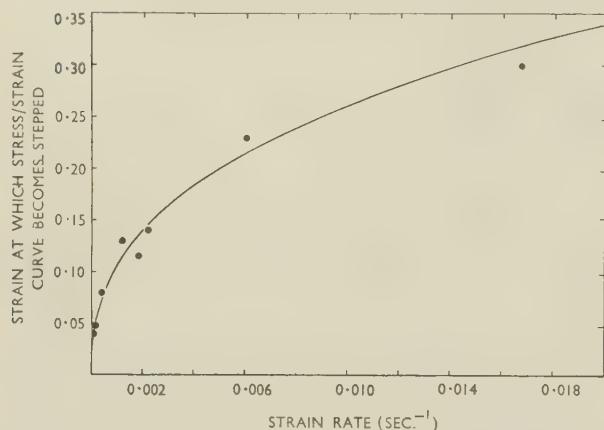


FIG. 3.—The Effect of the Speed of Testing on the Strain at Which Steps Appear on the Stress/Strain Curve of 70:30 Brass.

zinc atoms through the copper lattice must also be increased for steps to appear on the stress/strain curve. Cottrell's hypothesis suggests that this will occur only when the density of vacancies has increased, i.e. at a higher strain. Fig. 2 shows a curve obtained when the strain rate was increased twice

during the course of a test. Increasing the strain rate smooths out the stepped curve until a higher strain is reached, when the steps reappear. Cottrell's rough calculations suggest that the relation between strain rate and the strain at which the steps appear should be linear. Fig. 3, however, shows that the relation is more parabolic. If Cottrell's hypothesis is correct in principle, this finding suggests that either the rate of diffusion of zinc atoms is not directly proportional to the density of vacancies or that the number of vacancies formed is not proportional to the plastic strain.

It is not thought that strain-ageing in annealed 70:30 brass of this grain-size (0.055 mm.) is of any industrial significance, as no surface markings ("stretcher strains") could be seen on the specimens. Any markings which might have appeared during the later stages of the tests, when the steps in the stress/strain curve were fairly large, were masked by "orange-peeling" of the surface. However, if the specimens were first cold rolled (20–30%), surface markings could be seen. They were not very pronounced and resembled the type-B markings seen in aluminium alloys.⁵ No signs of a reduction in ductility due to strain-ageing could be observed in this brass. This is in agreement with the work of Polakowski on tin bronze.⁶

This work is part of the research programme of the Mechanical Working Division of the British Iron and Steel Research Association.

REFERENCES

1. C. F. Elam, *Proc. Roy. Soc.*, 1927, [A], **116**, 694.
2. R. Ergang, *Metal Ind.*, 1952, **81**, 261.
3. G. W. Ardley and A. H. Cottrell, *Proc. Roy. Soc.*, 1953, [A], **219**, 328.
4. A. H. Cottrell, *Phil. Mag.*, 1953, [vii], **44**, 829.
5. V. A. Phillips, A. J. Swain, and R. Eborall, *J. Inst. Metals*, 1952–53, **81**, 625.
6. N. H. Polakowski, *ibid.*, 1952–53, **81**, 617.

MICROSTRUCTURES OF ALUMINIUM BRONZES.

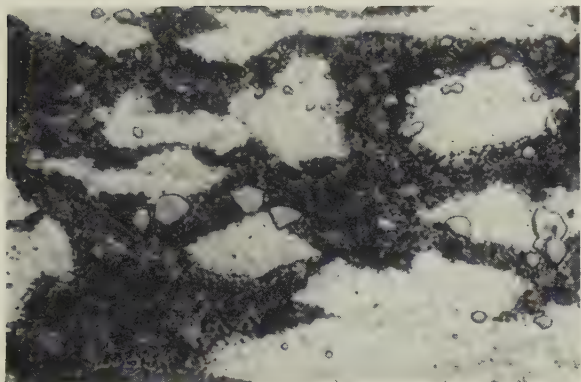


FIG. 12.—9.63% Al. Hot rolled at 900° C. and air-cooled. α (white) and κ (relief) in matrix of partially transformed β . $\times 1250$.

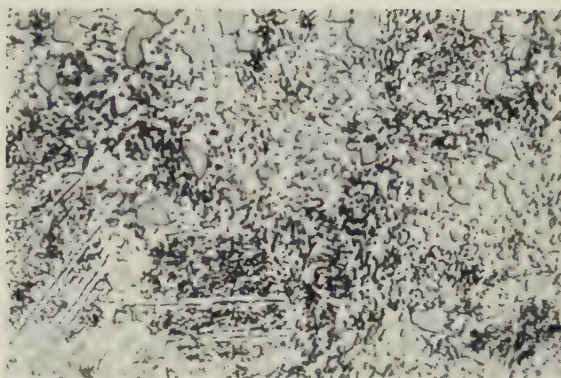


FIG. 13.—10.6% Al. Hot rolled at 850°–900° C., air-cooled, lightly cold rolled with intermediate and final anneals of 1 hour at 700° C. $\alpha + \kappa$. $\times 1500$.



FIG. 14.—10.5% Al. Rapidly cooled from $(\beta + \kappa)$ field. Acicular α in partially transformed β matrix. $\times 100$.

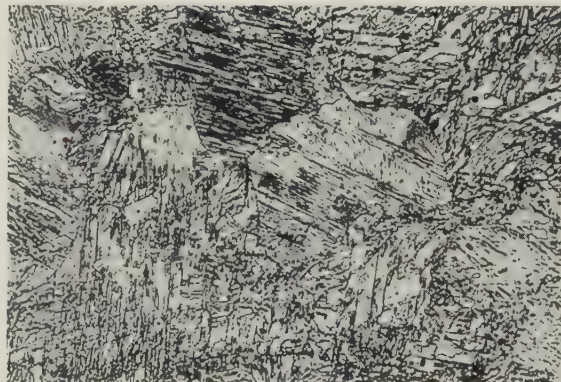


FIG. 15.—11.6% Al. Quenched from 900° C. κ in acicular β . $\times 100$.

Etched in 30 parts acetic acid, 20 parts nitric acid, and 30 parts acetone.

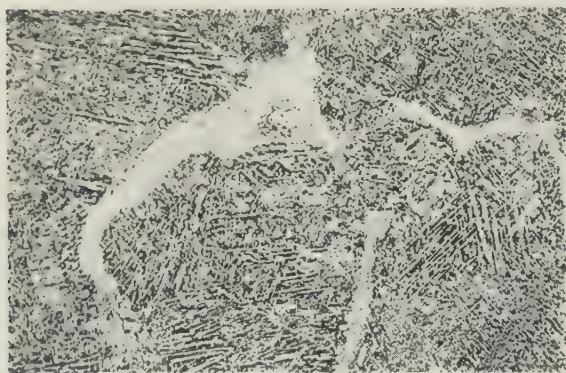
β TRANSFORMATION IN ALUMINIUM BRONZES.

FIG. 16.—9.11% Al. Quenched from 1050° C., followed by 1 min. at 900° C. $\times 100$.



FIG. 17.—10.62% Al. Quenched from 1000° C., followed by 1 min. at 850° C. $\times 100$.

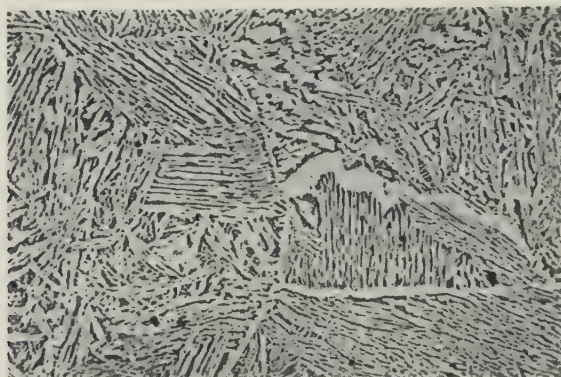


FIG. 18.—9.11% Al. Quenched from 1050° C., followed by 10 min. at 900° C. $\times 100$.

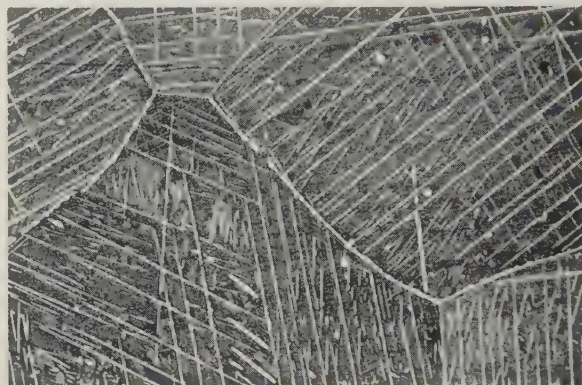


FIG. 19.—10.62% Al. Quenched from 1000° C., followed by 10 min. at 850° C. $\times 100$.

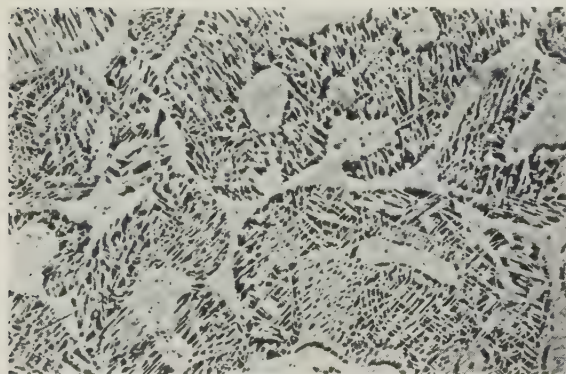


FIG. 20.—9.11% Al. Quenched from 1050° C., followed by 40 min. at 900° C. $\times 100$.

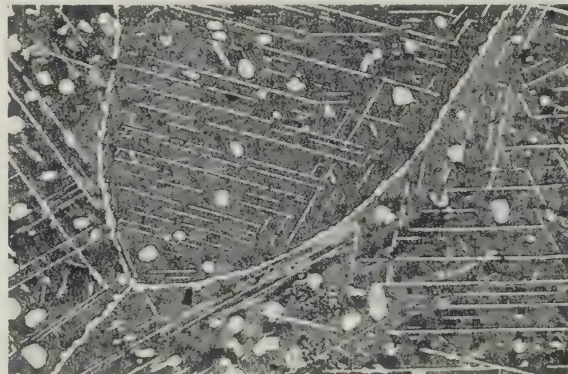


FIG. 21.—10.62% Al. Quenched from 1000° C., followed by 40 min. at 850° C. $\times 100$.

Etched in 20 g. ferric nitrate, 20 g. ammonium nitrate, 2 c.c. nitric acid, 500 c.c. water.

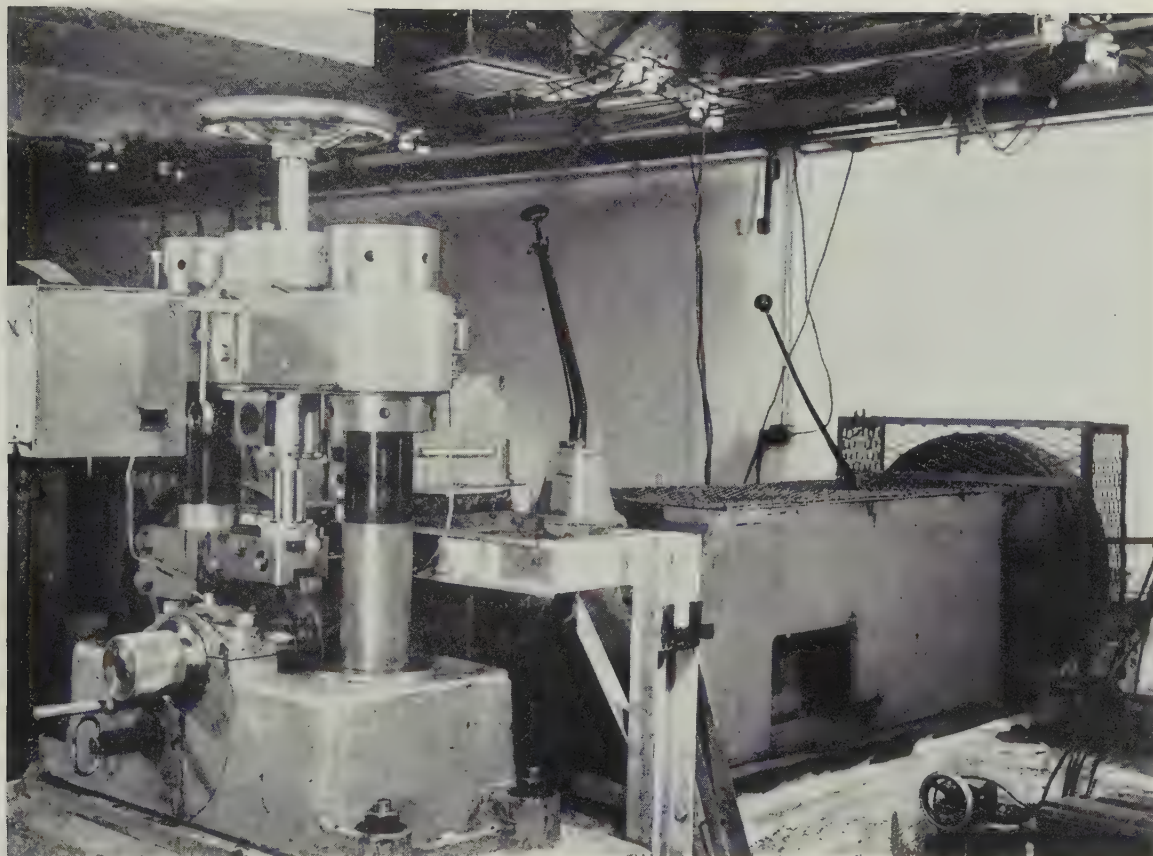


FIG. 1.—General View of the Plastometer with the Guard-Ring Box, Containing the Specimen, in Position.

SELECTIVE OXIDATION EFFECTS IN NICKEL-CHROMIUM ALLOYS.

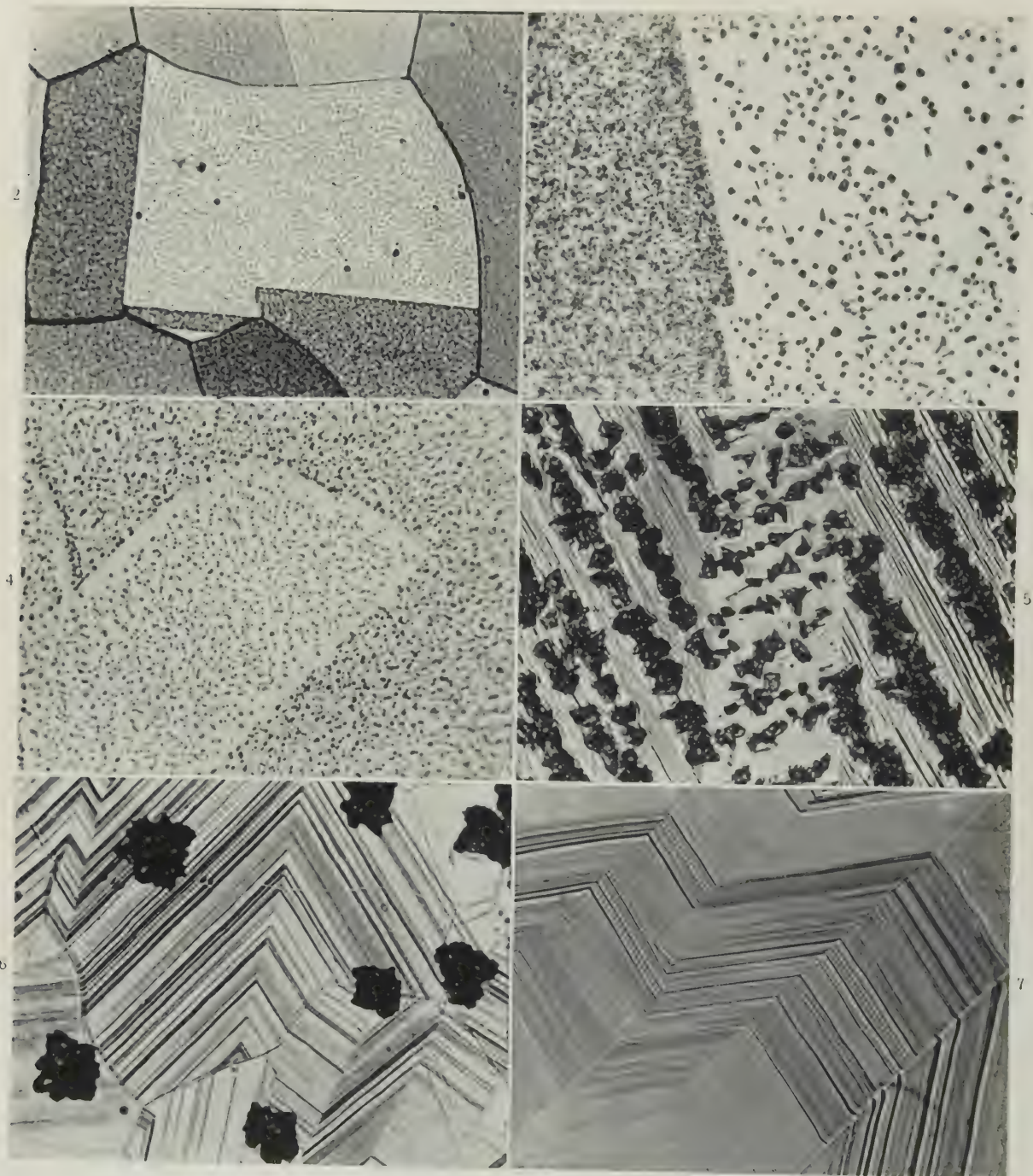
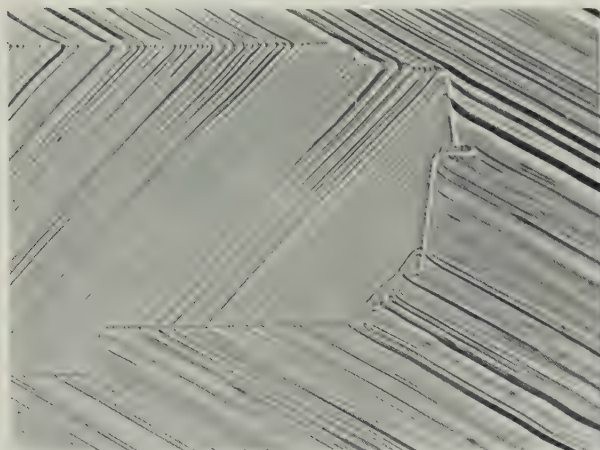
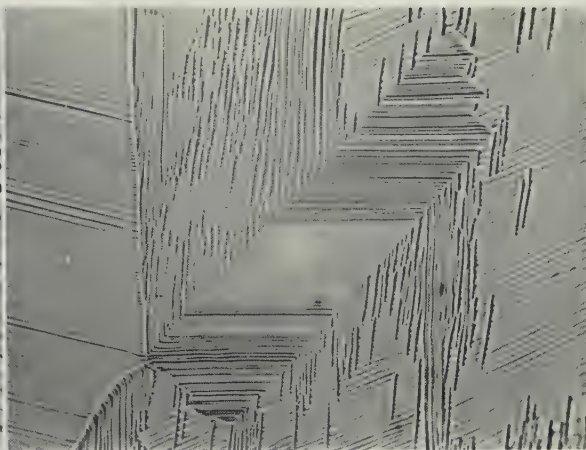
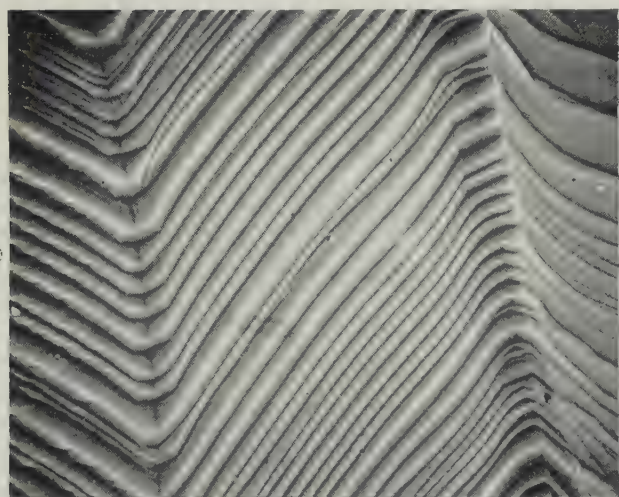


FIG. 2.—Region I. Primary nucleation. $p_{H_2O} : p_{H_2} = 6.5 \times 10^{-3}$; 900°C . $\times 100$.
 FIG. 3.—Same conditions as in Fig. 2. $\times 600$.
 FIG. 4.—Region II. Nucleation and recrystallization. $p_{H_2O} : p_{H_2} = 6.5 \times 10^{-3}$; 1040°C . $\times 400$.
 FIG. 5.—Region III. Coalescence of oxide. $p_{H_2O} : p_{H_2} = 2.4 \times 10^{-2}$; 1200°C . $\times 600$.
 FIG. 6.—Region IV. Striations on the metal surface. $p_{H_2O} : p_{H_2} = 3.3 \times 10^{-2}$; 1200°C . $\times 100$.
 FIG. 7.—Same conditions as in Fig. 6. $\times 400$.

(All reduced by $\frac{1}{2}$ in reproduction.)

SELECTIVE OXIDATION EFFECTS IN NICKEL-CHROMIUM ALLOYS.

FIG. 8.—Same conditions as in Fig. 6. $\times 600$.(Reduced by $\frac{1}{3}$ in reproduction.)FIG. 9.—Same conditions as in Fig. 6. $\times 400$.FIGS. 10-13.—Region IV. Electron Micrographs of Striations on the Metal Surface. $\times 2500$.
(Reduced by $\frac{1}{10}$ in reproduction.)

SELECTIVE OXIDATION EFFECTS IN NICKEL-CHROMIUM ALLOYS.

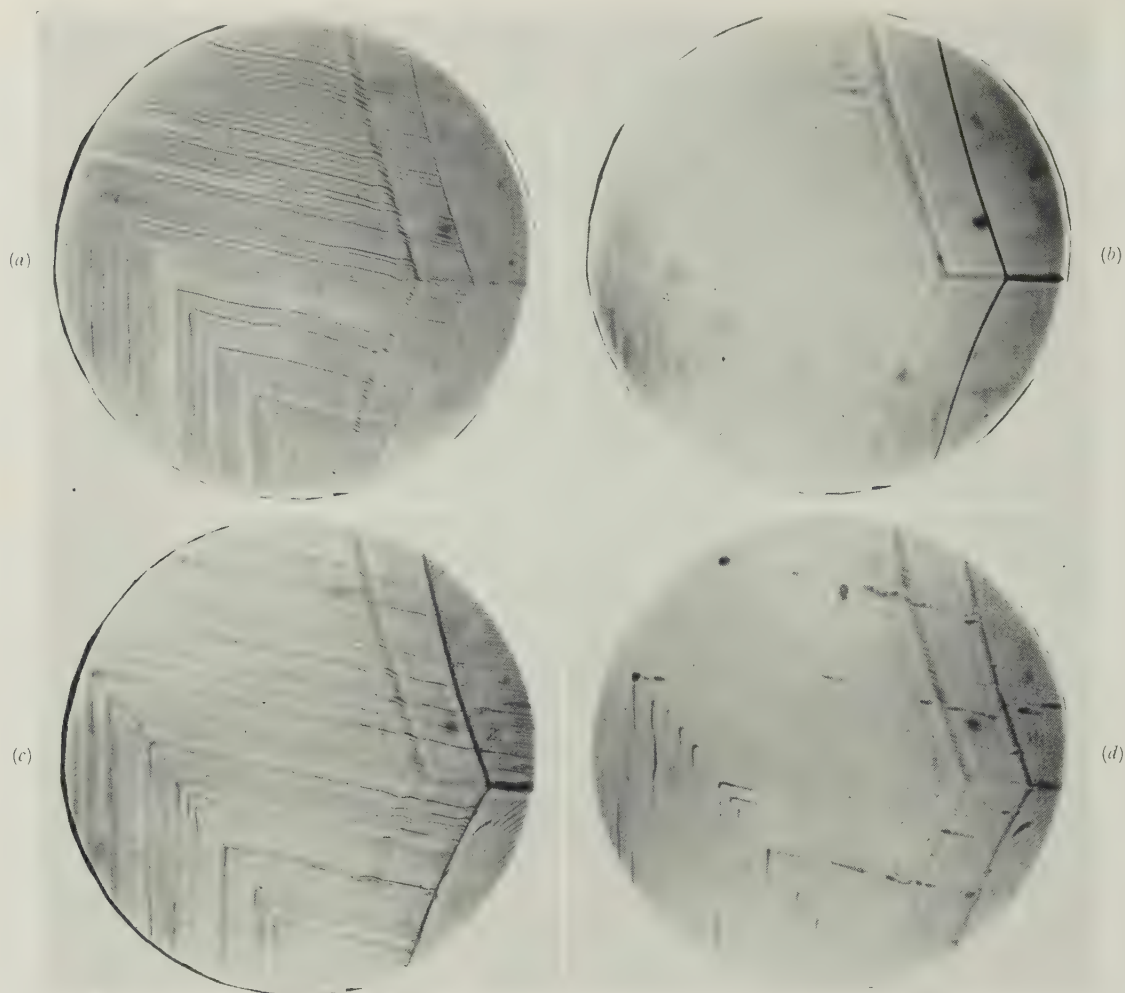


FIG. 14.—Illustrating Appearance and Disappearance of Striations on the Metal Surface After Treatment in Various Atmospheres. $\times 450$.

- (a) 60 min. at 1200°C .; $p\text{H}_2\text{O} : p\text{H}_2 = 3.3 \times 10^{-2}$. (b) 10 min. at 1200°C . in pure hydrogen.
 (c) 30 min. at 1200°C .; $p\text{H}_2\text{O} : p\text{H}_2 = 3.3 \times 10^{-2}$. (d) 10 min. at 1040°C . in pure hydrogen.

(Reduced by $\frac{1}{3}$ in reproduction.)

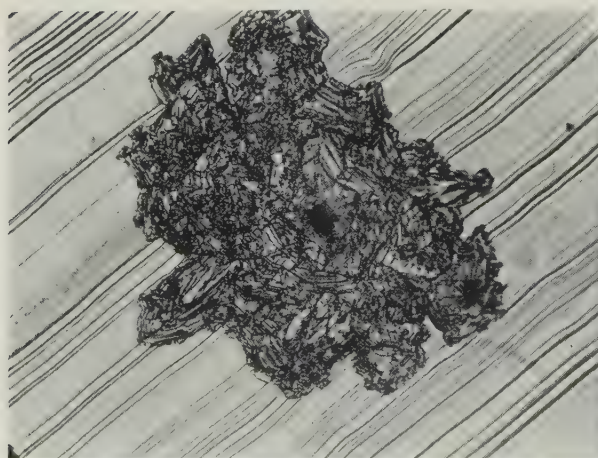


FIG. 15.—Region IV. Islands of Cr_2O_3 . $\times 600$.

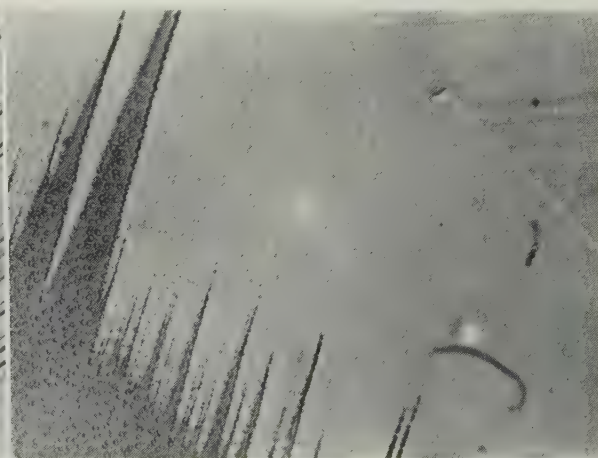
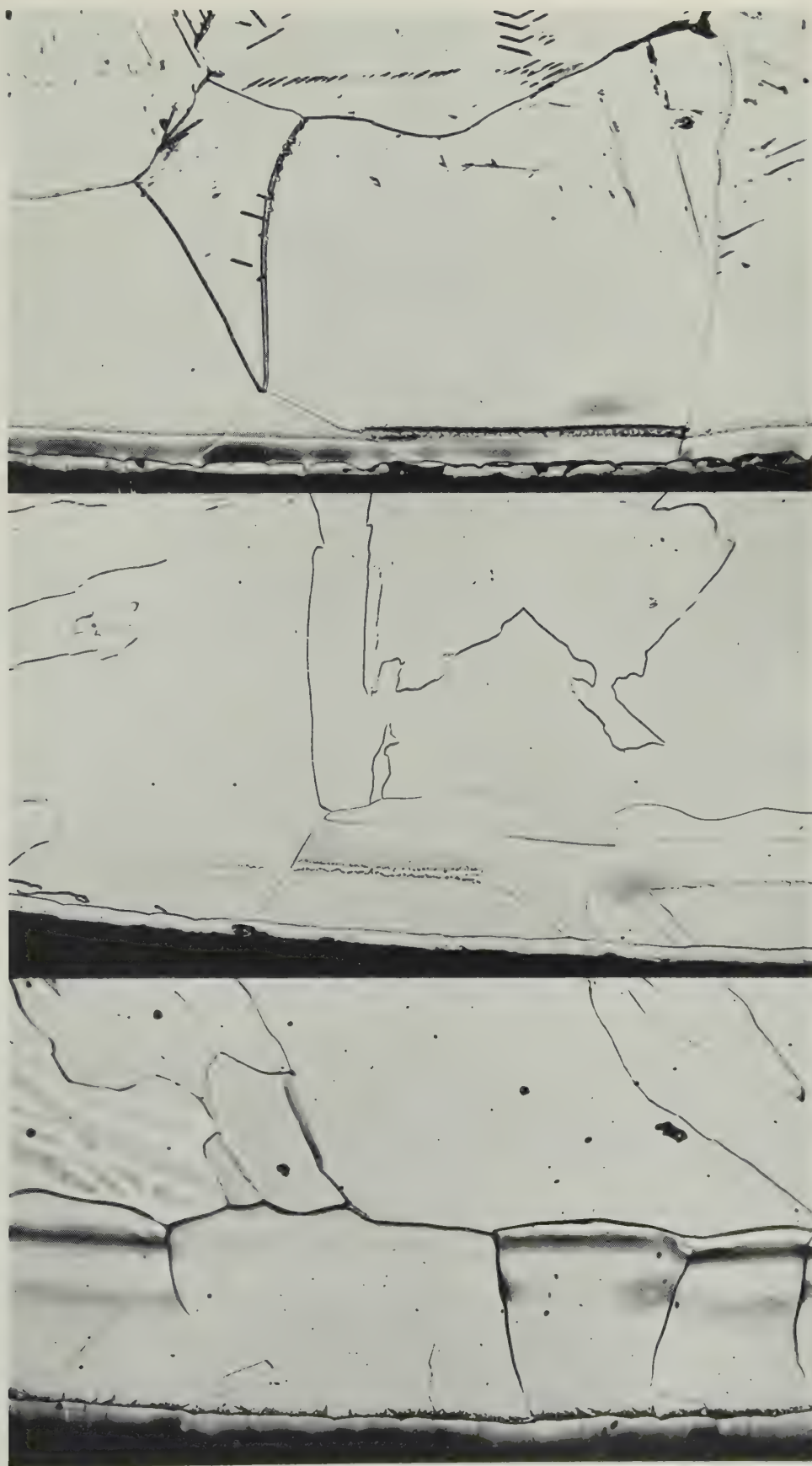


FIG. 16.—Region IV. Disappearance of Initial Oxide Layer and Appearance of Striations. $\times 600$.

(Reduced by $\frac{1}{6}$ in reproduction.)



FIGS. 5, 6, 7. Surface Layers Formed on Titanium After Reaction with Nitrogen. Etched in 3:1:1 glycerol: HNO_3 : HF . 250.

FIG. 6.—44 hr. at 950° C.

FIG. 7.—72 hr. at 850° C.

FIG. 5.—69 hr. at 1060° C.

STRUCTURES FORMED IN BINARY COPPER-ALUMINUM EUTECTOID ALLOY AT VARIOUS STAGES OF TRANSFORMATION.

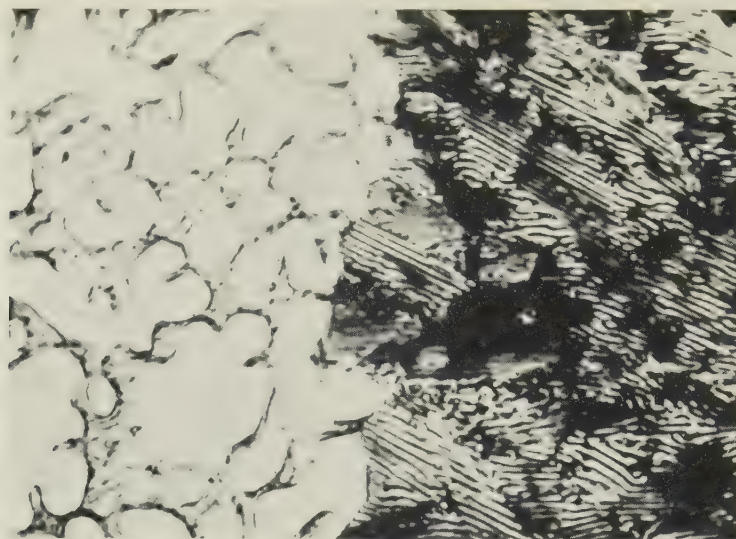


FIG. 1.—15 min. at 515° C. Eutectoid is growing into the $\beta + \beta_1$ matrix. Note the correlation between the pseudomorphs of the $\beta + \beta_1$ structure in the eutectoid and the adjacent $\beta + \beta_1$. $\times 2000$.

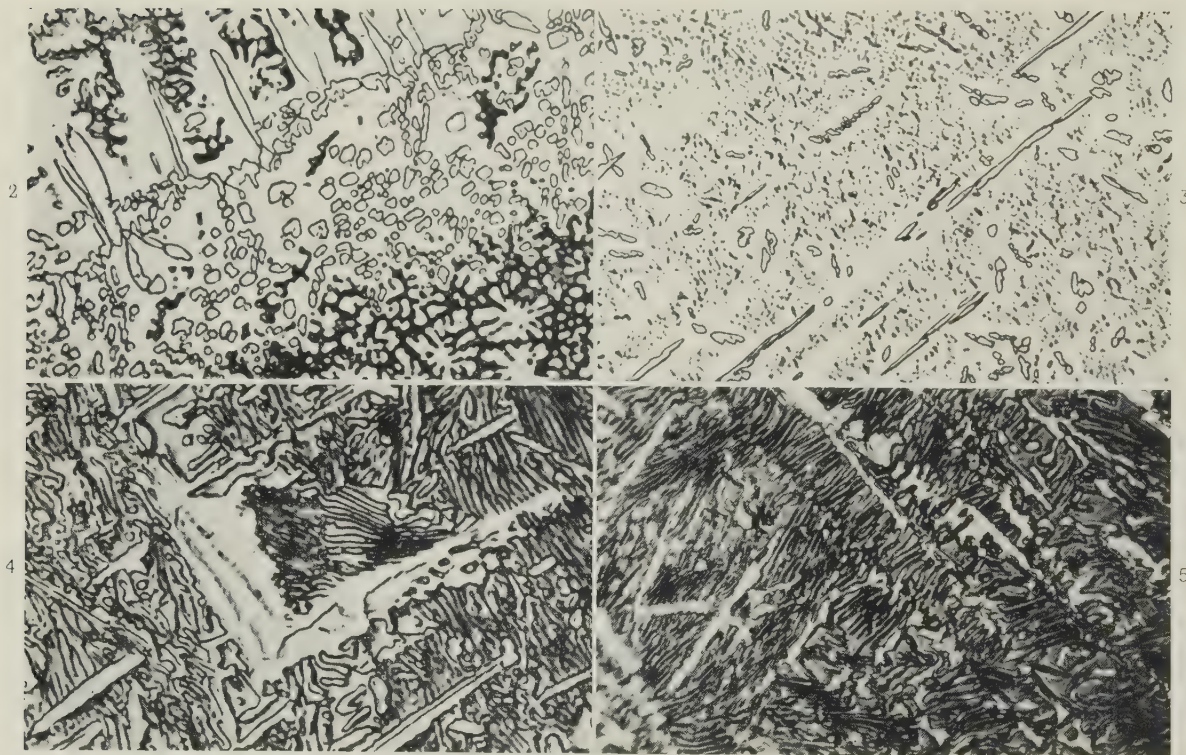


FIG. 2.—2 min. at 500° C. Grain-boundary α surrounded by β_1 . The general matrix is $\beta + \beta_1$ and β is dark-etching. $\times 1200$.

FIG. 3.—8 min. at 515° C. Pro-eutectoid α is surrounded by a sheath of β_1 . The matrix, which is mottled in appearance, is $\beta + \beta_1$. $\times 275$.

FIG. 4.—Nearly 5 days at 400° C. Cored pro-eutectoid α is being absorbed by eutectoid. $\times 1500$.

FIG. 5.—Completely transformed at 400° C. Irregularities in the structure of the eutectoid are due to the absorption of α needles by eutectoid. $\times 1500$.

CORROSION-FATIGUE PROPERTIES OF AN ALUMINIUM-MAGNESIUM-SILICON ALLOY IN THE UNPROTECTED, ANODIZED, AND PAINTED CONDITIONS *

1575

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SYNOPSIS

The endurance strength of a fully heat-treated aluminium alloy of the H10 type has been determined in air and when subject to the action of distilled water, ordinary tap-water, and a 3% sodium chloride solution. The endurance strength of the alloy was much reduced in the presence of these liquids, the corrosion-fatigue strength in Birmingham or London tap-water being about half that in air, whilst the corrosion-fatigue strength in the salt solution was only 25% of the fatigue strength in air.

Anodizing afforded an appreciable measure of protection against corrosion-fatigue effects, although the fatigue strength in air of the anodized metal was rather lower than that of the unprotected metal. Painting in accordance with a carefully specified schedule gave extremely effective protection even under the most severe corrosion-fatigue conditions, the fatigue strength of the painted material in the salt solution being rather better than that of the unprotected material tested in air.

I.—INTRODUCTION

THE lightness and generally good corrosion-resistance of aluminium and certain of its alloys have resulted in an increasing use of these metals in the engineering and transport industries. In some of these applications the material may be called upon to withstand alternating or repeated stresses and, at the same time, be subject to a corrosive environment. Much of the previous work on the corrosion-fatigue resistance of aluminium alloys has been carried out on those of the Duralumin type, and the amount of similar experimental data on alloys of the H10 type, now used for a variety of engineering purposes in this country, is rather scanty. In an endeavour to gain an increased knowledge of the properties of this important group, a series of fatigue and corrosion-fatigue tests has been made on a selected H10 alloy in the unprotected, anodized, and painted conditions, using distilled water, two different supply waters, and a 3% sodium chloride solution as the corroding media.

II.—EXPERIMENTAL

1. MATERIAL USED

The alloy studied in all the tests was an aluminium-magnesium silicide alloy containing Cu 0.07, Fe 0.20, Mn 0.58, Mg 0.61, Si 0.94%, Ti trace. It was obtained in the form of a single billet 30 in. long \times 7 $\frac{3}{4}$ in. in dia., cast by a semi-continuous direct-chill

machine. After heating to 500° C. the billet was extruded at an outgoing speed of 25 ft./min. through a four-hole die, to produce four rods each 82 ft. in length \times $\frac{5}{8}$ in. in dia., but, for the tests described in the paper, only the middle 50 ft. of each rod were used. After cutting into the shorter lengths re-

TABLE I.—*Tensile and Hardness Properties of Extruded and Fully Heat-Treated, Direct-Chill Cast H10 Rod.*

Position in Central 50 Ft. of Extrusion	Limit of Proportionality, tons/in. ²	0.1% Proof Stress, tons/in. ²	Ultimate Tensile Strength, tons/in. ²	Elongation, %		D.P. Hardness (10-kg. load)
				On 2 in.	On 4√A	
Front	19.2	23.8	25.4	14	19 $\frac{1}{2}$	125
Back	19.2	24.2	25.9	13	18	125
Front	19.1	24.7	26.2	13	17 $\frac{1}{2}$	126
Back	20.2	23.8	25.1	12	17 $\frac{1}{2}$	122
Front	21.5	24.8	26.8	14	17	124
Back	21.0	24.1	25.8	13	16 $\frac{1}{2}$	122

quired, and before machining the requisite test-pieces, the material was solution-treated in a salt bath at 525° C. for $\frac{1}{2}$ hr. and artificially aged at 160° C. for 18 hr., after which it was allowed to cool in air. The macrostructure in the heat-treated condition is illustrated in Fig. 1 (Plate XXI). The black circle indicates the area of material contained in the cross-section of the reduced portion of both the fatigue and the tensile test-pieces.

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The tensile properties were determined for each of the 50-ft. rods after heat-treatment, test-pieces conforming to B.S. 18 and having a gauge dia. of 0.282 in. being used. The tensile-test results are given in Table I, and it will be noted that these conform to the usual specification for this type of material (B.S. 1476 (HE10)).

$\frac{1}{2}$ hr. in either (a) boiling water, or (b) boiling 5 wt.-% potassium dichromate solution. After the sealing treatment, all specimens were well washed in cold water.

Specimens to be painted were: (i) degreased in trichlorethylene vapour, (ii) given a proprietary chromating treatment which produced a surface

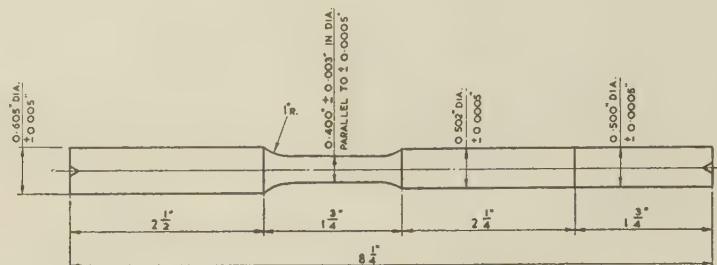
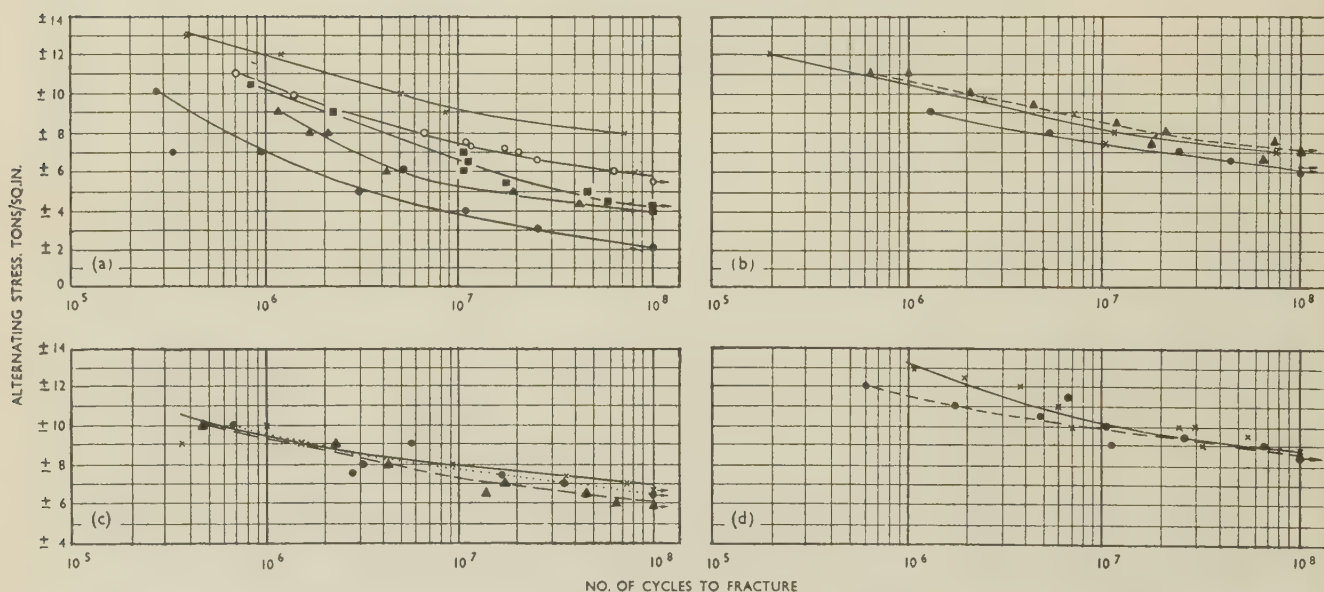


FIG. 4.—Form and Dimensions of Fatigue-Test Specimen.



FIGS. 5 (a)-(d).—Results of Corrosion-Fatigue Tests on Extruded and Heat-Treated H10 Rod. (a) Not protected; (b) anodized and hot-water sealed; (c) anodized and sealed in potassium dichromate; (d) painted.

KEY.

× Air. o Distilled water. ■ Birmingham tap-water. ▲ Metropolitan Water Board tap-water. • 3% sodium chloride solution.

2. PREPARATION OF FATIGUE-TEST SPECIMENS

The form of the fatigue-test specimen is shown in Fig. 4. The machined surfaces of all specimens, including those subsequently protected, were finished by emerying until all circular tool marks had been removed, the final paper being of "00" grade.

Specimens to be anodized were first degreased in trichlorethylene liquid and then anodized in accordance with specification D.T.D. 910B under the following conditions: bath composition 20 vol.-% H_2SO_4 , bath temperature $20^\circ C.$, 12.5 V., time of treatment $\frac{1}{2}$ hr. After washing in cold running water for $\frac{1}{2}$ hr., the anodized specimens were sealed by immersion for

having excellent paint-holding and anti-corrosive properties, (iii) cold-water rinsed, (iv) given a warm rinse in water acidified to counteract the effect of any water-soluble salts, (v) dried, then painted with a coating of red oxide/chromate primer, (vi) after drying for 24 hr., given a spray coat of a well-known proprietary alkyd finishing paint. Both primary and finishing coats are widely employed by coachbuilders and in other branches of the transport industry.

3. FATIGUE-TESTING CONDITIONS

Specimens, prepared as described, were tested in a rotating-cantilever type of machine, illustrated in

Fig. 2 (Plate XXI), the speed of rotation being 5000 r.p.m. In this machine the load is so arranged that there is a uniform bending moment over the whole of the reduced parallel portion of the specimen. For tests in the presence of the various corrosive agents, the liquid was stored in an aspirator (shown in Fig. 1) from which it dropped continuously on to the reduced parallel portion of the specimen at the rate of approximately one drop/sec.

For each of the four different surface conditions—i.e. unprotected, anodized and sealed in boiling water, anodized and sealed in boiling dichromate, and painted—tests were made to determine the fatigue characteristics in air, and also the fatigue characteristics when the following corrosive agents were present: (1) 3% sodium chloride (all surface conditions), (2) Metropolitan Water Board water (unprotected and anodized conditions), (3) Birmingham tap-water (unprotected condition only), and (4) distilled water (unprotected condition only).

The *S/N* curves covering these thirteen conditions of test are shown in Figs. 5 (a)–(d). Analyses of the Metropolitan Water Board and the Birmingham tap-waters are given in Table II.

TABLE II.—Analysis of Tap-Waters.

Origin	Metropolitan Water Board	Birmingham
Total dissolved solids:	p.p.m.	p.p.m.
Organic	47	15.8
Inorganic	315	34.6
Silica (as SiO ₂)	5.6	1.92
Aluminium, Iron	Not detected	Not detected
Calcium (as Ca)	107	6.71
Magnesium (as Mg)	4.1	1.4
Nitrates (as NO ₃)	2.5	0.14
Sulphates (as SO ₄)	49.2	5.7
Chlorides (as Cl)	30.3	9.9
Copper	0.04	0.08
Total alkalinity (as CaCO ₃)	222	15
Total hardness (as CaCO ₃)	300	19
Dissolved carbon dioxide	Nil	5.5
pH value	8.0	7.6

III.—DISCUSSION OF RESULTS

Figs. 5 (a)–(d) show that in general, it is not possible to quote an endurance strength independent of the number of stress reversals, since all the curves are still falling quite steeply even after 10^8 cycles. For this reason, in the discussion that follows, comparison between different treatments and conditions is based on the endurance strength corresponding to a life of 10^8 cycles. For rapid comparison the endurance strengths for the thirteen different test conditions are summarized diagrammatically in Fig. 6, from which it will be seen that the endurance strength of the unprotected material in air is ± 8 tons/in.². Under the action of either tap water, however, it drops to about ± 4 tons/in.². More serious still is the effect of the presence of the salt solution, the endurance strength falling to ± 2 tons/in.² or only 25% of the

value obtained under normal atmospheric conditions. An interesting point and one of some importance to be noted from Fig. 5 (a) is the significant loss in endurance strength in the presence of these corrosive media after even smaller numbers of cycles, e.g. 10^6 .

The data for the anodized material subjected to two different methods of sealing show that although in the presence of tap-water the corrosion-fatigue resistance is somewhat greater with hot-water sealing, dichromate sealing gives rather better results in the presence of the salt solution. Broadly speaking, however, the protection afforded by anodizing is equally efficacious for both methods of sealing. That anodizing is an effective method of protection is clearly shown in Fig. 6, since the endurance strength

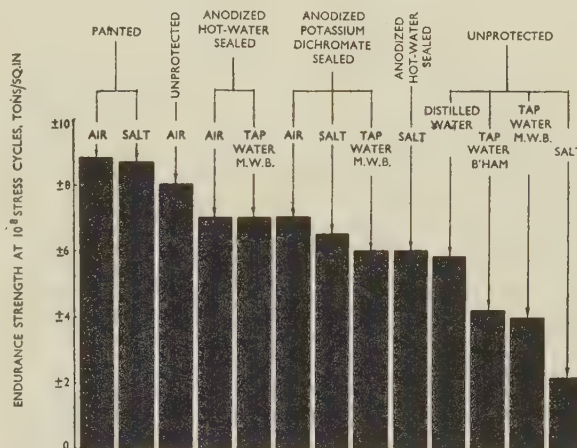


FIG. 6.—Summary of Endurance Strength of Extruded and Fully Heat-Treated H10 Rod Under Various Test Conditions.

under exposure to salt water is ± 2 tons/in.², as against ± 8 tons/in.² for the unprotected metal under the same conditions. It is interesting to note that whilst the salt solution was much more deleterious than the two supply waters in the case of the unprotected metal, the effects of all three were very much the same with the anodized metal. It is also noteworthy that the fatigue strength in air of the anodized material is distinctly less than that of the unprotected material in air. Results by other workers on this particular aspect have varied somewhat, but several investigators have reported a decrease in fatigue strength in air due to anodizing.^{1, 2, 3}

The present finding that anodizing actually reduces somewhat the fatigue strength in air was supported by microscopic examination, which revealed small surface defects in the anodized layer; these presumably act as stress-raisers under the subsequently applied alternating-stress conditions. However, even if anodizing results in a small but definite reduction in fatigue strength under ordinary air conditions, its extremely beneficial effect on the fatigue strength under corrosive conditions seems to be beyond question. Its favourable effect on the corrosion-fatigue resistance of other aluminium alloys has, of course, been previously demonstrated by Gerard and Sutton.⁴

The protective value of the paint coating was assessed by two conditions of testing only, viz., in air and in the presence of the salt solution. From Fig. 6 it can be seen that painting affords very substantial protection against the detrimental influence of the salt solution, the endurance strength being nearly ± 9 tons./in.² for both conditions of testing. The strength of the painted material in air is only slightly higher than that of the unprotected alloy, indicating that some minor corrosion-fatigue effects are, in fact, experienced owing to corroding influences under atmospheric air conditions. The considerable protective value of the paint has, however, been amply demonstrated by these corrosion-fatigue tests in the most severe medium employed.

IV.—MICROSCOPIC EXAMINATION

From each of the thirteen test conditions at least one specimen was selected, after test, for detailed microscopic examination. The direction of fracture proved to be in general at right angles to the longitudinal axis of the specimen and all fractures, no matter what corrosive agent was present, were predominantly transcrystalline in character. This is particularly interesting, since the common experience with the material in question is that, if corrosion takes place, it is of an intercrystalline character.

A typical subsidiary fatigue crack is shown in Fig. 3 (Plate XXI). This photomicrograph was taken from a test-piece after exposure to Birmingham tap-water, but microscopic examination of a large number of other specimens showed that the corrosive medium had no influence on the general characteristics of the fracture. This detailed microscopic examination, considered to be a most important part of the investigation, suggests that the presence of the corrosive agent during testing accelerated failure but did not in any way change the type of failure. This finding is, of course, in line with generally accepted views on corrosion-fatigue,^{5, 6} which postulate that the role of the corrosive agent is to form a pit which acts as a stress-raiser and that the resulting increase in stress may cause further breakdown of any protective film with deepening of the pit and a heightening of stress. In this way the stress and the effects of the corrosive agent are mutually intensifying.

V.—CONCLUSIONS

The conclusions of the investigation may be briefly summarized as follows:

(1) The fatigue strength of a fully heat-treated H10 alloy is very much reduced by the presence during test of such relatively mild corrosive agents as distilled water and normal supply waters, e.g. the corrosion-fatigue strength in Birmingham or London tap-water is about half the fatigue strength in air.

(2) The reduction in fatigue strength in the presence of a more severe corrosive agent (3% salt solution) is very considerable, and the corrosion-fatigue strength in this medium is only 25% of the fatigue strength in air.

(3) Anodizing affords a considerable measure of protection against corrosion-fatigue effects, but the ordinary atmospheric fatigue strength of the anodized material is not as high as that of the unprotected material.

(4) Painting in accordance with a carefully specified schedule gives extremely effective protection under the most severe corrosion-fatigue conditions; even in a 3% salt solution the fatigue strength is rather better than that of the unprotected metal tested in air.

(5) All fatigue cracks are predominantly transcrystalline, and the type of cracking and the general mode of failure are not affected by the corroding medium.

ACKNOWLEDGEMENTS

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REFERENCES

1. W. Campbell, *J. Electrodepositors Tech. Soc.*, 1952, **28**, 273.
2. I. Igarashi and S. Fukai, *Trans. Soc. Mech. Eng. Japan*, 1940, **6**, (22), 12.
3. K. Matthes, *Jahrb. deut. Versuchsanst. Luftfahrt*, 1931, 439.
4. I. J. Gerard and H. Sutton, *J. Inst. Metals*, 1935, **56**, 29.
5. H. J. Gough, *Proc. Amer. Soc. Test. Mat.*, 1933, **33**, (II), 3.
6. D. J. McAdam, Jr., *ibid.*, 1927, **27**, (II), 102.

THE ELECTRODEPOSITION AND REFINING OF HIGH-GRADE CHROMIUM*

1576

By H. T. GREENAWAY,† B.Met.E.

SYNOPSIS

The production of electrolytic chromium containing 0.01–0.02 wt.-% (0.03–0.06 at.-%) oxygen and 0.002 wt.-% (0.007 at.-%) nitrogen as its major impurities is described, together with a hydrogen-reduction technique for reducing these values below the chemically detectable amounts, i.e. 0.005 wt.-% (0.015 at.-%) and 0.001 wt.-% (0.003 at.-%), respectively. Investigation of the variables affecting electrodeposition of chromium from chromic acid baths indicated an optimum bath temperature of 83° C. and a chromic acid: sulphate ratio of rather less than 100. High-frequency induction heating was used in the hydrogen-reduction process, and a non-recirculatory system was found satisfactory.

I.—INTRODUCTION

AN earlier paper¹ described a method of producing electrolytic chromium containing 0.05 wt.-% (0.15 at.-%) oxygen as its major impurity. Since the publication of this work, a need has arisen for a higher grade of chromium, and the problem has been solved by: (a) the production of a purer electrolytic chromium containing 0.01–0.02 wt.-% (0.03–0.06 at.-%) oxygen and 0.002–0.005 wt.-% (0.007–0.019 at.-%) nitrogen, and (b) the adoption of a technique for the reduction of the oxygen and nitrogen content by hydrogen treatment. The latter has been found to yield chromium with oxygen and nitrogen contents below chemically detectable limits, i.e. 0.005 wt.-% (0.015 at.-%) oxygen and 0.001 wt.-% (0.003 at.-%) nitrogen. These two developments are described in the present paper.

In addition to the production of higher-purity chromium by the electrolytic method, an investigation was made into the possibility of increasing the current efficiency of the process. As is shown below, the current efficiency of this type of bath (containing hexavalent chromium and with an acidity of pH 4) is inherently low; no major increase could therefore be expected, but it was hoped that a significant improvement could be achieved by variations in technique. The effect of varying the following plating conditions was therefore investigated: bath composition, current density, bath temperature, and time of plating.

II.—ELECTROLYTIC PRODUCTION OF CHROMIUM

1. APPARATUS

The plating bath used in the earlier work¹ to produce chromium containing 0.05 wt.-% oxygen consisted essentially of a lead-lined tank contained in an

electrically heated water-jacket. Temperature was controlled by a glass-sheathed thermostat in conjunction with a hot-wire vacuum switch. The levels in the bath and in the heating jacket were kept constant by two constant-head water tanks. The cathode was a $\frac{5}{8}$ -in. copper tube, the anode a lead cylinder 7 in. in dia. and 6 in. high. The acid bath and lead anode were made from pure lead, since antimonial lead was found to contaminate the electrodeposit with approximately 0.2% antimony. Polyvinyl chloride tubing was used for "stopping-off" the cathode, as the commercial waxes available were unsuitable.

One modification of this bath has been made in order to reduce the consumption of chromic acid. Operation of the bath results in considerable gas evolution at both electrodes, and this, in conjunction with the high temperatures employed, leads to a considerable loss of chromic acid spray into the exhaust duct. This was originally of the order of 10 lb. of chromic acid for every pound of chromium deposited. This loss has now been reduced to less than 1 lb. of chromic acid per pound of chromium by the use of a glass bell which covers both the cathode and anode and dips below the surface of the electrolyte. The cathode enters the bell through a narrow neck.

2. PURITY OF ELECTROLYTIC CHROMIUM

The investigations¹ into the effect of changes in plating conditions on the purity of chromium produced, and on the current efficiency of the process, have been extended. The plating conditions varied are temperature, time, current density, and bath composition.

Tables I–IV give some representative results obtained. The current-efficiency values are based on the weight of chromium recovered from the copper cathode. This weight does not include the nodules of chromium which form on the deposit, particularly

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during the longer times of plating, and fall to the bottom of the plating bath.

TABLE I.—Effect of Temperature of Plating.

Run No.	Plating Conditions :			Bath Composition :		Oxygen,* wt.-%	Current Efficiency, %
	Temp., °C.	Time, hr.	Current Density, amp./ft. ²	CrO ₃ , g./l.	SO ₄ , g./l.		
99	72	75	880	290	3.65	0.12	6.5
8	80	70	1100	271	3.61	0.06	6.1
41	83	78	1100	280	3.75	0.02	5.3
92	87	72	880	241	4.02	0.01	5.0

* The methods used for determining the oxygen and nitrogen values quoted in this paper have been described elsewhere.²

The results given in Table I are very significant in connection with the present work. They show that the oxygen content can be reduced from 0.12 to 0.01 wt.-% simply by raising the temperature from 72° to 87° C. There is, however, an associated slight fall in current efficiency. Temperatures in excess of 87° C. were not investigated for two reasons :

- The graph of oxygen content against temperature appears to be flattening out above 83° C.
- There were practical difficulties associated with the use of higher temperatures, particularly excessive fuming.

Table II indicates that relatively high current efficiencies are obtained in the first few hours of plating, an effect which is not readily understood.

TABLE II.—Effect of Time of Plating.

Run No.	Plating Conditions :			Bath Composition :		Oxygen, wt.-%	Current Efficiency, %
	Temp., °C.	Time, hr.	Current Density, amp./ft. ²	CrO ₃ , g./l.	SO ₄ , g./l.		
97	72	3.5	880	297	3.70	0.10	13.5
98	72	24	880	297	3.70	0.12	8.0
99	72	75	880	290	3.65	0.12	6.5
9	80	1	1100	268	3.51	0.12	14.0
10	80	4	1100	268	3.51	0.10	10.1
7	80	24	1100	274	3.61	0.07	7.3
8	80	70	1100	271	3.61	0.06	6.1
94	84	3.5	880	339	4.04	0.03	11.0
100	83	48	880	285	3.65	0.02	6.2
93	84	72	880	289	4.14	0.02	6.3

The realization of these good values is not very practical unless the chromium can be automatically removed from the cathode at short intervals, or unless some type of moving-strip cathode can be employed. Neither alternative is particularly attractive, at least for laboratory-scale operations.

From Table III it would appear that the reduction of current density from 1100 to 880 amp./ft.² results in a slight increase in current efficiency. In this connection, it was noticed that nodule formation was slightly greater when operating at the higher current density, and presumably more nodules of chromium

fell from the deposit under these conditions than was the case at the lower current densities. This could at least partially explain the low current efficiencies (calculated from the weight of chromium recovered from the cathode) obtained at the higher current density. The effects of variations in current density on oxygen content are not great, although the oxygen content does fall with current density for those electrodeposits containing higher percentages of oxygen.

The results of this work differ considerably from those obtained by Brenner, Burkhead and Jennings.³ These workers found that a reduction of current density resulted in a decrease in current efficiency and an increase in oxygen content. However, the conditions employed in the two investigations differ

TABLE III.—Effect of Current Density.

Run No.	Plating Conditions :			Bath Composition :		Oxygen, wt.-%	Current Efficiency, %
	Temp., °C.	Time, hr.	Current Density, amp./ft. ²	CrO ₃ , g./l.	SO ₄ , g./l.		
40	80	80	1100	250	2.7	0.08	5.6
38	80	80	880	260	2.73	0.05	7.1
41	83	78	1100	280	3.74	0.02	5.3
42	83	90	880	283	4.4	0.02	7.1

in one significant detail. Brenner *et al.* worked on deposits 0.002–0.010 in. thick, while the study now described was carried out on deposits 0.06–0.12 in. in thickness. The present investigation has shown (see Table II) that current efficiency and, to a lesser extent, oxygen content are both dependent on the thickness of the electrodeposit, and hence Brenner's results cannot readily be used for comparison.

TABLE IV.—Effect of Bath Composition.

Run No.	Plating Conditions :			Bath Composition :			Oxygen, wt.-%	Current Efficiency, %
	Temp., °C.	Time, hr.	Current Density, amp./ft. ²	CrO ₃ , g./l.	SO ₄ , g./l.	Ratio CrO ₃ : SO ₄		
31	80	90	1100	410	2.77	148	0.38	1.0
33		53	1100	406	3.63	112	0.18	4.9
3		67	1100	200	2.05	97.6	0.06	4.8
30		95	1100	346	4.18	83	0.05	4.9
8	82	70	1100	271	3.61	75	0.06	6.1
68		78	880	227	3.61	63	0.03	7.5
50		90	880	140	2.66	52.7	0.12	6.3
46		78	1000	200	4.50	44.5	0.15	7.8
86	83	54	880	290	3.28	88.4	0.02	6.4
63		90	880	396	5.02	78.8	0.02	6.7
41		78	1100	280	3.75	74.7	0.02	5.3
67		78	880	323	4.93	65.6	0.03	6.7
56		90	1000	262	4.77	54.9	0.05	6.9

Table IV illustrates the importance of bath composition. For low oxygen values the sulphate content must be kept reasonably high, i.e. the CrO₃ : SO₄ ratio must be less than the usual figure of 100 employed in commercial chromium plating. This is demonstrated by runs 3, 8, and 30, where the resulting

oxygen content of 0.05–0.06% is the best obtainable at the plating temperature of 80° C. In contrast, run 31 shows that a high $\text{CrO}_3 : \text{SO}_4$ ratio results in a high oxygen content (0.38%) and a low efficiency (1%), and run 33 illustrates the same point to a lesser degree. On the other hand, the $\text{CrO}_3 : \text{SO}_4$ ratio should not be too low, otherwise high oxygen contents will result. This is shown by a comparison of runs 50 and 46 with run 68, which has the lowest oxygen content to be expected at 82° C. The bottom section of the table, referring to a bath temperature of 83° C., further illustrates this point, since it shows that an oxygen content of 0.02% is not attained until a $\text{CrO}_3 : \text{SO}_4$ ratio of approximately 70 is exceeded. Sulphate content has another effect in that nodule formation is more troublesome in baths with both high and very low sulphate contents.

Summarizing, the following are the chief effects of variations in plating conditions on the electrodeposition of chromium:

(1) The oxygen content can be reduced to as low as 0.01% by increasing the temperature of the bath to 87° C.

(2) Bath composition plays an important part in determining both oxygen content and current efficiency.

(3) Reasonably high current efficiencies (i.e. above 8%) associated with low oxygen contents do not appear to be obtainable, except for short plating times.

(4) Current density is not critical, but the lower current densities do give slightly better current efficiencies.

The bath conditions now being employed in the author's laboratory, chosen on the basis of the above work, are:

Bath composition	{ 300 g./l. chromic acid,
Temperature	4 g./l. sulphate
Current density	83° C.
Plating time	880 amp./ft. ²
	80–90 hr.

These conditions are consistently producing chromium containing 0.02% oxygen and 0.002% nitrogen at a current efficiency of approximately 7%. Two baths are in continuous production, operating from 60- and 250-amp D.C. rectifiers, respectively. Cathodes are changed twice weekly to prevent excessive nodule formation. The cylindrical deposits obtained from one bath are 5 in. long, $\frac{5}{8}$ -in. bore, about 0.1 in. thick, and weigh approximately 100 g.; while those obtained from a larger bath are 10 in. long, 1-in. bore, about 0.1 in. thick, and weigh approximately 400 g.

3. ELECTROCHEMICAL CONSIDERATIONS

The reasons for the low current efficiency of the electrodeposition of chromium from hexavalent baths (of acidity pH 4) are best understood by reference to the pH/potential diagram for chromium given in Fig. 1. This is a simplified version of the diagram due to Pourbaix,⁴ and shows that there are three major factors which make cathodic reduction of

hexavalent chromium ions to chromium metal a process of low efficiency.

(1) The hydrogen deposition overvoltage on copper is -0.2 V., bringing the potential for hydrogen deposition on copper at pH 4 down to -0.4 V. This value is significantly more positive than that at which chromous ion deposition would be expected to take place (i.e. -0.7 V.), and hydrogen evolution will start before chromium ion deposition begins, and will continue along with the latter process. The hydrogen evolution is considered to be mainly responsible for the low current efficiency of the plating process. Methods for reducing hydrogen evolution all necessitate increasing the hydrogen overvoltage. This may

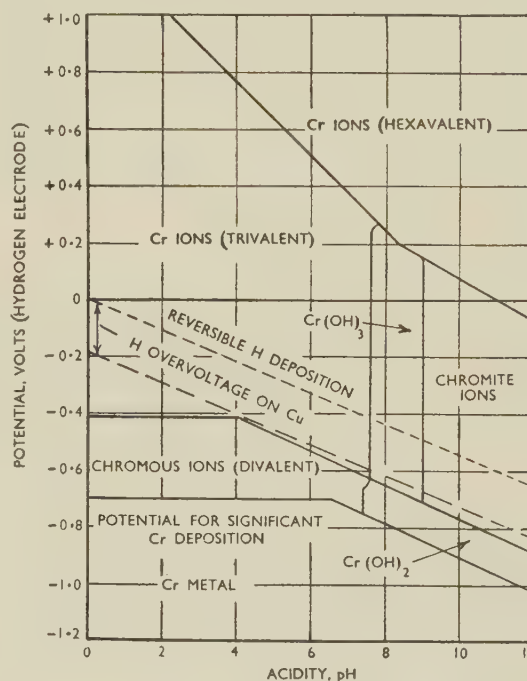


FIG. 1.—pH/Potential Relationships of Chromium.
(After Pourbaix.⁴)

be done by changing the cathode material—lead has a much larger overvoltage than copper—but this would prove only a temporary expedient, as excessive hydrogen evolution would begin as soon as the cathode became covered with chromium, which has a small overvoltage (slightly less than that of copper).

(2) The reduction process itself is inefficient, as six electrons must be used to reduce hexavalent ions to chromium metal, whereas if a trivalent salt were used, only three electrons would be required.

(3) With hydrogen evolution taking place at the cathode surface, the pH of the catholyte will be increased beyond 4, and partial passivation of the cathode surface by precipitation of the hydroxides Cr(OH)_3 or Cr(OH)_2 may occur. This process will make areas of the cathode inactive, so lowering the cathode efficiency. It might also lead to the inclusion of hydroxy compounds in the chromium plate, which

would explain those cases where high-oxygen chromium is deposited at low current efficiency.

The trivalent chromium bath has not been used in the present work, although its current efficiency is several times that obtained in the hexavalent bath, because it is much more complicated and produces chromium with a high oxygen content.

III.—HYDROGEN-REDUCTION TREATMENT OF ELECTROLYTIC CHROMIUM

A further requirement in the author's laboratory was for chromium containing less oxygen and nitrogen than in the electrolytic product described above. Hydrogen reduction was selected as the best means of achieving this end. The method was used as early as 1924 by Rohn⁵ and by Adcock⁶ in 1927. In more recent years it has been chosen by Kroll, Hergert, and Yerkes,⁷ by Gilbert, Johansen, and Nelson,⁸ and by Sully, Brandes, and Mitchell⁹ to reduce the oxygen content of chromium powder. These workers employed temperatures between 1000° and 1500° C., with

a 20-kW. high-frequency heating unit. This method of heating has the following advantages:

(a) Within the furnace enclosure, only the chromium itself is heated to any extent. This enables high temperatures to be used without danger of contamination from the refractory ware.

(b) The times of heating and cooling can be considerably shortened by comparison with treatment in, say, a platinum-wound resistance furnace, where thermal shock must be avoided to ensure reasonable furnace life. Apart from the saving in time, this has another advantage. The deoxidation reaction, $6H + Cr_2O_3 \rightleftharpoons 3H_2O + 2Cr$ is reversible and tends to go to the left at lower temperatures. Slow heating and cooling will therefore hold the chromium for a considerable time at those temperatures where oxidation (rather than deoxidation) can occur, and are to be avoided.

(3) The hydrogen in the present work was not recirculated. Earlier workers have claimed that

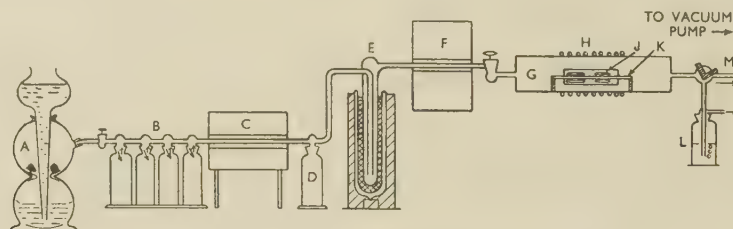


Fig. 2.—Diagram of Hydrogen-Reduction Apparatus.

times ranging from several days at the lower temperatures to a few hours at 1500° C. The hydrogen was specially purified and in most cases recirculated through the system. The higher working temperatures were generally preferred, since a greater content of water vapour in the gas stream could then be tolerated and the time at temperature reduced.

However, the temperature of reduction was in many cases kept low in order to avoid silicon contamination of the chromium. This occurred as a consequence of the reduction by hydrogen of silica in the furnace refractories to volatile silicon monoxide which reacted with the chromium to form Cr_2O_3 and chromium silicide ($CrSi$). This reduction is known to take place rather rapidly above 1300° C. In some cases silicon contamination was avoided by lining the furnace tube with alumina, the chromium to be reduced being held in boats of the same material.

The hydrogen-reduction technique to be described varies in the following details from those employed by the workers mentioned above:

(1) Instead of working on powdered material, complete electrodeposited tubes of chromium are treated. The powdering operation, with its possibility of contamination, is thus avoided.

(2) The tubes are heated by induction, employing

recirculation is necessary to maintain the hydrogen at a sufficient level of purity; but the "open-circuit" technique described below was found to be satisfactory and simpler than that used previously. It must, however, be admitted that it consumes more hydrogen than does the recirculating system, and can be expected to be useful in small-scale work only.

Fig. 2 gives a diagrammatic illustration of the hydrogen production and purification train employed in this work, and of the chromium-heating technique employed. Hydrogen is generated in the Kipp's apparatus (A), passes through the drying bottles (B) containing caustic soda, magnesium perchlorate, and phosphorus pentoxide, and is then deoxidized by copper turnings contained in a clear silica tube heated to 400° C. in the furnace (C). Final drying is carried out in the magnesium perchlorate bottle (D) and the dry-ice trap (E). Titanium, contained in a recrystallized alumina tube and heated to 1350° C. in the furnace (F), is used for final deoxidation and also for removal of nitrogen.

After passing through its purification train, the hydrogen enters the glazed silica tube (G), around which is wound the induction coil (H). The charge of chromium (J) is held in the centre of the induction coil by two tungsten rods (K) passing through the

chromium. The gas leaves the silica tube via the bubbler (*L*). An outlet (*M*) is provided for evacuating the whole apparatus. All joints are made from glass or metal waxed together, no rubber being employed. Charges of 600 g. are used. These consist of one chromium tube 10 in. long, 1-in. bore, into which are inserted two tubes each 5 in. long, $\frac{5}{8}$ -in. bore.

The hydrogen-reduction technique is as follows. After the whole system is evacuated and checked for leaks, hydrogen is passed through, and the copper and titanium furnaces brought to temperature. The chromium is heated to 1500° C., the temperature being read with an optical pyrometer sighting through a window mounted in the end of the silica tube (*G*). The gas flow is regulated to 3–4 bubbles per second and heating times of 3–4 hr. are employed. This is found to reduce the oxygen and nitrogen contents to less than the chemically detectable amounts (i.e. 0.005 and 0.001 wt.-%, respectively). Chemical analysis

TABLE V.—Results Obtained with Hydrogen-Reduction Apparatus.

Starting Material		Treatment, hr. at 1500° C.	Product	
O ₂ , wt.-%	N ₂ , wt.-%		O ₂ , wt.-%	N ₂ , wt.-%
0.11	0.002	3.5	0.02	<0.001
0.11	0.002	4	<0.005	0.001
0.12	...	3	0.02	<0.001
0.12	...	4	<0.005	<0.001
0.05	...	3	<0.005	<0.001

failed to detect any silicon contamination from the silica tube. The analytical method employed was capable of detecting 0.002 wt.-% silicon. The Brinell hardness number of this chromium is approximately 110.

A few early runs were made using a platinum-

wound furnace instead of the induction heater, the chromium being contained in an alumina boat. This apparatus successfully reduced the oxygen and nitrogen contents, although there appeared to be some surface contamination by alumina. No aluminium, however, could be detected chemically.

Table V gives some typical results obtained using the hydrogen-reduction technique.

These results show that even high oxygen contents (0.12 wt.-%) can be nearly eliminated provided the treatment time is not less than 4 hr.

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REFERENCES

1. H. T. Greenaway, S. T. M. Johnstone, and M. K. McQuillan, *J. Inst. Metals*, 1951–52, **80**, 109.
2. H. L. Wain, F. Henderson, and S. T. M. Johnstone, *ibid.*, 1954–55, **83**, 133.
3. A. Brenner, P. Burkhead, and C. Jennings, *J. Research Nat. Bur. Stand.*, 1948, **40**, 31.
4. M. J. N. Pourbaix, "Thermodynamics of Dilute Aqueous Solutions", p. 103. 1949: London (Edward Arnold and Co.).
5. W. Rohn, *Z. Metallkunde*, 1924, **16**, 275.
6. F. Adcock, *J. Iron Steel Inst.*, 1927, **115**, 369.
7. W. J. Kroll, W. F. Hergert, and L. A. Yerkes, *J. Electrochem. Soc.*, 1950, **97**, 258.
8. H. L. Gilbert, H. A. Johansen, and R. G. Nelson, *Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197**, 63.
9. A. H. Sully, E. A. Brandes, and K. W. Mitchell, *J. Inst. Metals*, 1952–53, **81**, 585.

1577 THE FABRICATION OF CHROMIUM AND SOME DILUTE CHROMIUM-BASE ALLOYS *

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SYNOPSIS

Arc-melted electrolytic chromium can be fabricated by forging, swaging, and rolling. Forging and swaging were carried out at 900° C., and rolling in the temperature range 400°–900° C. As-deposited electrolytic chromium of sufficient purity, and with an electropolished surface, is shown to be ductile at room temperature after heating to 850° C., which removes internal stresses, considerably reduces the hydrogen content, and produces grain growth in the deposit. This material remains ductile after arc casting and after the various fabricating processes mentioned above, provided that contamination is reduced to a minimum.

Alloys of chromium containing 1 wt.-% titanium and up to 5 wt.-% tungsten can be fabricated by the methods used for pure chromium, and the products are ductile at room temperature. However, this technique was not successful with higher alloy contents.

I.—INTRODUCTION

CHROMIUM metallurgy is currently of interest principally because of the successful development of chromium-base alloys possessing excellent creep-resistance at temperatures of the order of 900° C.,¹⁻³ and therefore having a potential application of great importance as gas-turbine blade materials. The major disadvantage of these alloys from the practical point of view is that they are almost invariably brittle and unforgeable. At the time these alloys were developed, chromium itself had not been produced in a form showing significant ductility at room temperature. However, this has now been achieved, and some of the factors influencing room-temperature ductility have been evaluated.⁴ The production of chromium ductile at room temperature considerably enhances the possibility of making ductile and workable chromium-base alloys with significant strength at high temperatures.

Several investigators⁵⁻¹⁰ have reported that chromium can be worked at elevated temperatures, but details of the methods used and the properties of the fabricated material have frequently been meagre. The present paper describes the production, from electrolytic chromium, of forged bar, swaged rod, and rolled strip which are ductile at room temperature. The structure and some of the properties of the material at each stage of fabrication are given, and the application of the methods developed for pure chromium to some dilute binary chromium-base alloys is mentioned.

II.—EXPERIMENTAL PROCEDURE

The equipment used in the various fabricating operations was in general standard, and is referred

to in the appropriate sections. Indications of room-temperature ductility were obtained in a simple three-point bend test, in which the specimen rested on two $\frac{1}{8}$ -in.-dia. steel rollers placed $\frac{5}{16}$ in. apart and was bent at a strain rate of approximately 0.25 in./min. by a screw-loaded plunger having a $\frac{1}{16}$ -in.-radius cylindrical nosepiece. The normal specimen dimensions were approximately $0.5 \times 0.25 \times 0.03$ in., although some larger specimens of swaged rod (up to 0.135 in. dia.) have been tested. Bend-test specimens were usually electropolished in order to produce a surface as free as possible from notches. Electropolishing was carried out in a bath consisting of 64% orthophosphoric acid, 15% sulphuric acid, balance distilled water, using a current density of 12 amp./in.². The bath was initially at room temperature, but the temperature rose considerably during polishing. This bath has been found to give a metallographic finish on chromium over a considerable range of bath composition, current density, and temperature.¹¹

III.—ELECTROLYTIC CHROMIUM

All the chromium used in this work was prepared by the electrolysis of chromic acid. For most of the experiments, a material having the following chemical analysis was used: oxygen 0.06 wt.-% (0.19 at.-%), nitrogen 0.005 wt.-% (0.019 at.-%); and no metallic impurities were detected in a spectrographic analysis. A note on the analytical methods used for the determination of oxygen and nitrogen in chromium is given elsewhere.⁴ The conditions governing the production of chromium of this purity have already been described.¹² It has recently been shown¹³ that these contents can be reduced to 0.01–0.02 wt.-% (0.03–0.06 at.-%) oxygen and 0.002 wt.-% (0.007

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at.-%) nitrogen, respectively, by control of the bath conditions, and that a high-temperature hydrogen-reduction treatment can lower these values to below the limits of chemical analysis. As mentioned below, samples of these two purer grades of chromium were used for some of the work.

As-deposited chromium plate containing approximately 0.02 wt.-% oxygen and 0.002 wt.-% nitrogen was brittle at room temperature even if electropolished. This was also true of less pure material. It is known¹⁴ that as-deposited chromium is characterized by the following features:

- (a) A high hydrogen content.
- (b) High internal stresses.
- (c) A very small grain-size.
- (d) Oxide networks.

It is further known that relief of internal stresses appears to occur at temperatures of the order of 300° C., and that hydrogen is largely removed in the temperature range 400°–600° C., depending on the time of heating. Grain growth has been found to begin between 400° and 700° C. The oxide films are more easily isolated from chromium heated to approximately 500° C., than from as-deposited material,¹⁵ and the work of Adcock¹⁶ and, more recently, of Sully and his co-workers,² indicates that further agglomeration of the oxide tends to occur on heating to 800° C. and higher.

Attempts to produce room-temperature ductility in as-deposited chromium by heating to 450° C. to remove hydrogen and internal stresses were unsuccessful. However, electropolished as-deposited chromium containing 0.02 wt.-% oxygen and 0.002 wt.-% nitrogen was ductile at room temperature after heating to 850° C. in a vacuum. Electrolytic chromium containing more than these amounts of oxygen and nitrogen was brittle at room temperature after a similar treatment. In the purer deposit microscopic examination revealed that grain growth had begun after heating to 850° C., but no grain growth could be detected in less pure material.

As-deposited chromium which had been heated at 1500° C. in pure hydrogen was ductile at room temperature in both the electropolished and acid-etched conditions. As an illustration of the extent of the room-temperature ductility obtainable, specimens of this material could be bent, in the testing machine, to an angle of 90° in 6–7 sec. (i.e. as far and as fast as the machine could be operated). On removal from the machine, such specimens could be bent by hand to 180° in approximately half a second.

These results show that it is a comparatively simple matter to produce ductile electrodeposited chromium, provided that the material is sufficiently pure. It appears that in such material either grain growth or agglomeration of oxide-film networks is necessary for room-temperature ductility. In any treatment having these effects, hydrogen and internal stresses are automatically removed.

A complicating factor in these experiments on as-

deposited chromium was the existence of cracks. These sometimes formed during, or were revealed by, electropolishing, and seemed to bear no relationship to the oxide networks. Their origin is uncertain, but they may have been due to high internal stresses developing during the electrodeposition of the comparatively thick plate ($\frac{1}{16}$ – $\frac{1}{8}$ in.) used in this study, or they could have been the result of mechanical damage occurring during removal of the deposit from the cathode.

IV.—ARC MELTING

Electrolytic chromium was melted in a tungsten-arc furnace similar to that described by Geach and Summers-Smith.¹⁷ Melting was carried out in an argon atmosphere on a water-cooled copper hearth, using a D.C. current supply and a negative tungsten electrode, and the chromium was cast into approximately cylindrical ingots, 2 in. long and $\frac{3}{4}$ in. in diameter, in a suitably shaped depression in the hearth (see Fig. 2, Plate XXII). The argon atmosphere was purified by "gettering" with a small button of titanium before the chromium was melted. Spectrographic and vacuum-fusion analyses have been made on arc-melted chromium and compared with the as-deposited material. No significant metallic impurity was detected in either case, and, as shown in Table I, the

TABLE I.—*Effect of Arc Melting on Impurity Content of Chromium.*

Condition of Chromium	O ₂ , wt.-%	N ₂ , wt.-%	H ₂ , g./100 c.c.
As deposited . . .	0.1	0.04	110
Arc melted . . .	0.1	0.03	8

tendency was for arc melting to reduce the non-metallic impurity content. For this test, a sample was deliberately chosen which had relatively high oxygen and nitrogen contents, so that any change produced by arc melting would be more easily detectable.

This method of casting produced an ingot in which the grain structure was columnar, with the long axes of the columnar crystals in general normal to the furnace hearth, i.e. lying along a short axis of the specimen. A thin layer of equiaxed grains was usually formed on the surface of the ingot owing to the accelerated cooling rate. One interesting point regarding the arc-melted chromium ingots was that, if the material contained more than about 0.02 wt.-% oxygen and 0.002 wt.-% nitrogen the surface of the ingot had a metallic but etched appearance, whereas for purer material the surface was extremely bright and smooth (see Fig. 2). Apparently these impurities have a considerable influence on the surface tension of chromium. Microscopic examination revealed that the grain-size of the cast ingots was large, and that a number of oxide inclusions were present, both in the grain boundaries and forming a kind of sub-structure

within the grain (see Fig. 4, Plate XXII). The hardness of as-cast chromium was approximately 120 D.P.N. (10-kg. load).

The room-temperature ductility of as-cast chromium has been examined on longitudinal and transverse bend specimens cut from the ingot. Electropolished longitudinal specimens were invariably ductile provided that the material was sufficiently pure, but transverse specimens were sometimes brittle. This effect has not been studied very closely, but it could indicate that an orientation effect, similar to that observed in cast molybdenum,¹⁸ may exist for cast chromium. These results were complicated by the fact that specimens prepared from cast ingots for bend tests sometimes contained grinding cracks. This matter is under investigation.

For the production of the dilute chromium-tungsten and chromium-titanium alloys used in this work, high-purity tungsten and titanium powders were mixed with electrolytic chromium, and melted essentially as described for pure chromium. There appeared to be no macroscopic segregation of the alloying elements in the ingots and hardness readings across sections were uniform. Also, there was no evidence that grain refinement had been effected by the alloying additions.

As regards room-temperature ductility, chromium containing up to 5 wt.-% tungsten and a chromium-1 wt.-% titanium alloy were ductile in the as-cast condition provided that the specimens were electropolished. Chromium-10% tungsten material showed some evidence of room-temperature ductility, but a chromium-5% titanium alloy was brittle. However, in both these cases the situation was somewhat confused by the formation of grinding cracks.

V.—FORGING

Attempts were first made to forge cast chromium in air by heating the ingot to approximately 900° C. and hand-forging on an anvil. However, it was found that circumferential cracking leading to fracturing of the ingot invariably occurred before appreciable reduction in area took place. Moreover, it was not found possible to forge the fractured pieces of the ingot, since this resulted in further cracking. This fracturing appeared to occur along the columnar grain boundaries of the cast ingot, and, in an attempt to obviate this, the original cast structure of the ingot was broken up by forging in the manner illustrated in Fig. 1. The ingot was cut into two pieces, each approximately 1 in. long (Fig. 1 (a)), and each piece was then upset about 30% (i.e. forged normal to the long axis of the specimen, as in Fig. 1 (b)). This produced a disc which was forged along one of the circular axes, giving a bar as in Fig. 1 (c) which could be forged further as required. Forging in air did not seem to increase the oxygen content as revealed by the amount of oxide in the microstructure, except possibly in the extreme outer layers. This treatment refined

the as-cast grain structure, but the oxide network originally situated around the grain boundaries remained comparatively unaltered by forging. The hardness of chromium forged in air was approximately 130 D.P.N.

However, the difficulty with this procedure was that cracking started to develop at stage 1 (b), which resulted in fracture when the direction of forging was altered. An attempt to overcome this was made by separately sheathing the pieces cut from the cast ingot in mild steel and following the forging procedure as already described. Each piece of the cast ingot was ground and fitted inside a mild-steel round having an appropriate hole drilled in it, and a mild-steel plug was fusion-welded into the mild-steel round to complete the sheathing. No cracking or fracturing of the chromium occurred during forging at 900° C. in this

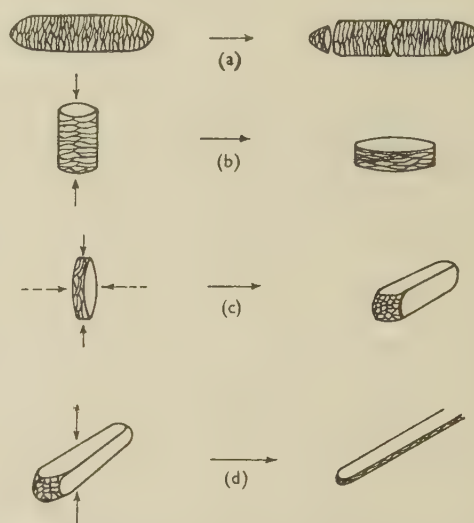


FIG. 1.—Schematic Representation of the Stages in Forging an As-Cast Ingot. The direction of forging in relation to the grain structure is indicated at each stage.

manner. However, if the initial upsetting operation was omitted, severe cracking along the dendrite boundaries resulted, as illustrated in Fig. 3 (Plate XXII). After the completion of forging, the mild-steel sheath could easily be removed in hot 1:1 HNO₃.

Electropolished samples of chromium forged in a sheath were ductile at room temperature, and the microstructure and hardness of the material were similar to that of chromium forged in air.

Previous attempts to hot-work highly alloyed chromium have been successful only with compositions containing a large proportion of a relatively low-melting metal, e.g. 35–45% iron,¹ and these alloys did not exhibit outstanding high-temperature properties. The working of dilute alloys has been effected by Kroll in 1936¹⁹ and more recently by Gilbert *et al.*²⁰ Apparently forging was not attempted or was not successful.

Preliminary tests have shown that chromium

alloys containing tungsten and/or titanium possess good creep properties, and in the present work effort was concentrated on these alloys. The ultimate objective was to shape by hot working alloys containing fairly large additions of these elements.

The addition of 1% tungsten did not cause any difficulties and forging at 900° C. in a mild-steel sheath was possible, but the 1% titanium and 5% tungsten alloys cracked on forging at this temperature. However, these alloys could be forged at 1200° C. provided that the mild-steel sheath was replaced by a nickel-chromium-molybdenum ferritic steel. Mild steel proved to be much too plastic at these temperatures.

Initially the 1% titanium alloy developed a pattern of very small surface cracks on forging. This cracking became less severe when the forging temperature was raised from 900° to 1200° C., and disappeared completely if the surface of the ingot was highly polished before sheathing. A 5% titanium and a 10% tungsten alloy could not be forged at 1200° or 1350° C. At the latter temperature only the sheath deformed, and the same result was obtained when a Nimonic 80A sheath was used. In a further attempt to forge these alloys, it was decided to heat the unsheathed ingots in a borax bath to the working temperature. The specimen was heated, removed quickly, and given one or two blows with the hammer, and then replaced in the bath until the forging temperature was again attained. It has since been found that Kroll¹⁹ had used this technique and that it has been patented recently for heat-resisting alloys.²¹

Pure chromium and the 1% tungsten alloy could be forged using this technique, but much higher forging temperatures were necessary than in the case of sheath-forging. Presumably the small specimens chilled quickly, so that forging was actually carried out at temperatures well below the bath temperature. Hardness values appear to indicate this. For example, the hardness of a 1% tungsten alloy worked at 900° C. by the bath technique was 233 D.P.N., compared with 188 D.P.N. for the sheathed alloy worked at the same nominal temperature. Owing to this cooling effect, it was not found possible to forge the more difficult alloys using a borax bath at 1200° C. At higher temperatures, the bath technique was unsatisfactory in that oxidation and contamination of the alloy became severe. At temperatures up to 1200° C. surface contamination was slight, probably owing to the fact that the oxide and nitride formed in the working period were fluxed in the heating period. Microscopic examination of chromium forged below 1200° C. revealed oxide penetration of only 0.001–0.003 in. Removal of this amount by electropolishing resulted in clean, bright surfaces.

Another technique was also tried, viz. heating to the forging temperature in an atmosphere of hydrogen. This had the advantage that any oxygen and/or nitrogen contamination brought about in the working period would be removed in the heating period. The 5% titanium and 10% tungsten alloys, however, cracked when a furnace temperature of 1450°–1500° C.

was employed. Once again the disadvantage was that chilling of the small specimens occurred prior to working.

VI.—SWAGING

Successful hot-swaging operations, using a No. 3A Standard Swage (maximum capacity $\frac{3}{4}$ in.), were carried out on chromium. The procedure was to grind the forged billet to a circular section for ease of sheathing and then to polish with 80 grit emery paper which minimized the formation of cracks and other surface defects. The billet was sealed in a mild-steel sheath in a similar manner to that previously described for sheathing as-cast ingots for forging. The swaging temperature was nominally 900° C. and a reduction in area of 15% between successive passes was found to be satisfactory. A larger reduction in area between passes tended to produce "fins" on the mild-steel sheath, which in turn could lead to gross surface defects and severe cracking in the chromium rod. Similar defects were produced in the chromium rod if the mild-steel sheath became excessively scaled. This was avoided by descaling after each pass. If these precautions were taken, the swaged rod, although having typical hammer marks on the surface, was almost invariably free from cracking or major surface defects.

Swaging resulted in a further refinement of the grain-size as compared to that of the forged material; the grain-size decreased slightly towards the centre of the rod, and the grains were elongated in the longitudinal direction (see Fig. 5, Plate XXII). The oxide particles were randomly disposed. The hardness of swaged rod increased with the amount of working at 900° C., e.g. rod swaged from $\frac{1}{4}$ - to $\frac{1}{8}$ -in.-dia. increased in hardness from 130 to 170 D.P.N. Swaged rod has been shown to be ductile at room temperature. For example, electropolished specimens 0.135 in. in dia. have been bent rapidly to 90° and similar specimens 0.75 in. long have been twisted through 360° (see Fig. 6, Plate XXII).

Several attempts have been made, using different swaging conditions, and temperatures as high as 1450°–1500° C., to produce swaged rod direct from arc-melted ingots. However, in all cases severe cracking occurred, similar to that found on attempting to forge ingots without first upsetting. A similar lack of success attended attempts to swage as-cast alloy ingots at 1300° C., even when the ingots were sheathed in Inconel.

VII.—ROLLING

Chromium could be successfully rolled in the temperature range 450°–900° C., using standard rolling equipment. The chromium was first sheathed in mild steel as for previous working operations, and the mild-steel sheath was itself enclosed in an outer stainless-steel jacket. The reason for this composite sheathing was that, under the conditions of severe deformation accompanying rolling, it was found that a

mild-steel sheath flowed much more than the chromium. The mild steel tended to become very thin and to scale and crack at high temperatures, so that the chromium strip had a very uneven surface. On the other hand, the working characteristics of stainless steel appeared to be very similar to those of chromium, which made it a better sheathing material from this point of view. Unfortunately, it was very difficult to remove the stainless steel from the rolled chromium. No chemical solution was found which would not attack the chromium, and, in the majority of cases, the two metals adhered so well that mechanical separation was impossible. The composite mild-steel/stainless-steel sheath was quite satisfactory, and, after rolling, the stainless-steel sheath could be removed mechanically and the mild steel by acid dissolution.

No attempt was made to adopt a standard reduction between rolling passes, as this did not seem to be at all critical. Also, quite severe deformations could be given by rolling in the temperature range mentioned above without the necessity for frequent intermediate annealing. An occasional intermediate annealing was given, more to stop excessive work-hardening and cracking of the stainless steel than of the chromium.

Rollled strip was produced from swaged rod and forged bar. In each case it was necessary to remove surface defects from the stock which would otherwise have been rolled into the strip. Rolling directly after forging without resheathing was unsatisfactory for this reason.

The hardness and microstructure of rolled strip depended, of course, on the precise treatment. However, in general, rolled strip was fine-grained, with the grains elongated in the rolling direction, and the amount of grain elongation increased as the rolling temperature decreased. The microstructure was frequently non-uniform, in that areas were present where the amount of deformation was apparently much less than normal (see Fig. 7, Plate XXII). The reason for this is obscure, but probably arises from the initially non-uniform grain structure of the cast ingot. Annealing rolled strip at 900°–950° C. produced recrystallization and an equiaxed grain structure. Typical hardness values of strip rolled at 900° C. and annealed at 900° C. after rolling were approximately 210 and 108 D.P.N. (1-kg. load), respectively, while strip reduced from 0.125 to 0.060 in. at 900° C. and from 0.06 to 0.015 in. at 400° C. had a hardness of approximately 230 D.P.N.

In general, chromium rolled in the range 450°–900° C. was brittle at room temperature after removal from the sheath, but became ductile if the outer layers were removed by dissolution in 1:1 HCl. The question of the brittleness of chromium is considered elsewhere,⁴ but from the fabrication point of view it is of interest to note that methods were devised to reduce embrittlement during rolling. These methods consisted of iron plating or copper plating the chromium before sheathing for rolling, or by sealing in the sheaths in an argon atmosphere rather than in

air. Before each plating operation the chromium was polished with fine emery paper and degreased in trichlorethylene. Iron plating was carried out in a 400 g./l. purified ferrous chloride solution at 60°–65° C. and a current density of 20 amp./ft.², and copper plating in a standard acid copper sulphate solution (CuSO₄·5H₂O 200 g./l., H₂SO₄ 40 ml./l.) at a current density of 25–30 amp./ft.² at room temperature. In each case the plated layer was built up to a thickness of approximately 0.05 in. Sealing under argon was done in the argon-arc furnace used for melting, with the addition of an adaptor in the hearth to hold the sheathed specimen in a vertical position. The furnace was evacuated, filled with argon, and the weld made under an argon pressure of slightly less than one atmosphere.

Typical amounts by which the rolled strips had to be reduced in thickness by etching before room-temperature ductility in a bend test was achieved, are given in Table II.

TABLE II.—*Reduction of Thickness of Rolled Strips Before Ductility was Achieved.*

All specimens rolled at 850° C.

Condition of Material	Thickness of As-Rolled Strip, in.	Amount Removed, in.	% of Original Thickness
Air sealed . .	0.065	0.025	38
Copper plated . .	0.066	0.006	9
Iron plated . .	0.064	0.004	6
Argon sealed . .	0.050	0.006	13

The actual amounts removed as shown in this table were not determined with any great accuracy, but it is clear that embrittlement during rolling was considerably reduced by these procedures. It is now standard practice to argon seal at all stages of fabrication.

The degree of room-temperature ductility which can be achieved in rolled chromium is quite considerable. For example, rolled strips of the order of 0.03 in. or thicker could be bent and twisted quite readily at room temperature (see Fig. 6, Plate XXII). Room-temperature tensile tests have also been made on small specimens machined from rolled strip. The specimens were approximately 2.5 × 0.175 × 0.025 in. and testing was carried out in a Tate–Emery testing machine. The applied load was measured with an accuracy of ±1 lb. by means of a proving ring, and the specimen elongations were determined by two Huggenberger extensometers fixed on opposite sides of the specimen. The gauge-length was 0.5 in. and the rate of loading 10,000 lb./in.²/min. The tensile properties of the specimen showing the greatest room-temperature ductility were: 0.2% proof stress 55,000, maximum stress 74,000 lb./in.²; elongation 15%. This specimen had been rolled at 600° C., with one intermediate anneal at 850° C., and the surface electropolished.

The only previous work on rolling chromium-base

alloys is that done by Kroll¹⁹ on sintered specimens, using a borax bath as described for forging in Section V. The technique described above for chromium was found to be successful for the rolling of chromium-1% tungsten alloys at 900° C. Cracking occurred in the 1% titanium and 5% tungsten alloys on rolling at 900° C. If the rolling temperature was raised to 1200° C., it was found that the mild-steel

and the 1% tungsten alloy, and none of the other alloys could be rolled without cracking.

VIII.—DISCUSSION OF RESULTS

The results of this work are summarized in Table III.

Dealing first with as-deposited chromium, the results show that this material is ductile at room

TABLE III.—*Summary of Results.*

Material	Condition	Temperature of Working, °C.	Workability	Room-Temperature Ductility in Bending	Hardness, D.P.N.
CHROMIUM					
Containing 0.06 wt.-% O ₂ , 0.005 wt.-% N ₂	As deposited	Brittle after heating to 850° C. in a vacuum and electropolishing	...
Containing 0.02 wt.-% O ₂ , 0.002 wt.-% N ₂	As deposited	Ductile after the above treatment	...
Containing O ₂ and N ₂ below limits of chemical analysis	As deposited and hydrogen-treated at 1500° C.	Ductile in both electropolished and etched conditions	...
	As cast	Ductile	120
	Forged	900	Workable	"	130
	Swaged	900	"	"	170
	Rolled	400-900	"	"	200-230
CHROMIUM-TUNGSTEN ALLOYS					
1% W	As cast	Ductile	124
	Forged	900	Workable	... *	204
	Swaged	900	"	... *	195
	Rolled	900	"	Ductile	188
	"	1200	"	"	158
5% W	As cast	Ductile	180
	Forged	900	Not workable	...	260
	"	1200	Workable	... *	203
	Rolled	1200	"	Ductile	214
10% W	As cast	Slightly ductile	...
	Forged	1500	Not workable
CHROMIUM-TITANIUM ALLOYS					
1% Ti	As cast	Ductile	154
	Forged	900	Not workable	...	229
	Rolled	900	"	...	237
	Forged	1200	Workable	... *	173
	Rolled	1200	"	Ductile	174
5% Ti	As cast	Brittle	...
	Forged	1500	Not workable

* Not tested for ductility.

inner sheath was squeezed out from between the alloy and the stainless steel, so that welding occurred and separation was impossible without cracking the alloy. However, substitution of a nickel-chromium-molybdenum ferritic steel for the mild steel made successful rolling of these alloys possible. All these alloys had been forged before rolling, and were ductile at room temperature after rolling.

Attempts were made to roll as-cast chromium and chromium-base alloys, using the salt-bath technique at a nominal temperature of 1200°-1250° C. Only occasional success was achieved with pure chromium

temperature provided that it is sufficiently pure and has been heated to temperatures of the order of 850° C. This treatment largely removes internal stresses and hydrogen and causes some grain growth to occur.

Pure chromium ingots, produced by arc melting electrolytic chromium, can be hot worked by conventional methods such as forging, swaging, and rolling. The products at each stage of fabrication are ductile at room temperature if the material is initially of a high degree of purity and if impurity pick-up during fabrication is reduced to a minimum. The work described was, of necessity, carried out on small

samples, but no difficulty is anticipated on increasing the scale of operations. It is realized that the sheathing technique would be unsatisfactory for the working of large ingots on a commercial basis. However, the use of a salt bath for heating to the required temperature should be satisfactory with larger ingots provided that it gives adequate protection from contamination during fabrication.

Alloys of chromium containing up to 5% tungsten and 1% titanium could be hot worked using the techniques developed for pure chromium, and the worked products were ductile at room temperature. However, alloys containing greater additions of these elements could not be worked by these methods owing to the difficulty of maintaining a sufficiently high actual working temperature because of the rapid cooling of the small specimens used on removal from the heating medium. The indications were that larger

specimens of these materials could probably be worked by these techniques. For higher alloying additions, however, it appears that some other working method, such as extrusion, may be necessary.

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REFERENCES

1. R. M. Parke and F. P. Bens, *Symposium on Materials for Gas Turbines* (Amer. Soc. Test. Mat.), 1946, p. 80.
2. A. H. Sully, E. A. Brandes, and (in part) A. G. Provan, *J. Inst. Metals*, 1952-53, **81**, 569.
3. W. L. Havekotte, C. T. Greenidge, and H. C. Cross, *Proc. Amer. Soc. Test. Mat.*, 1950, **50**, 1101.
4. H. L. Wain, F. Henderson, and S. T. M. Johnstone, *J. Inst. Metals*, 1954-55, **83**, (4), 133.
5. W. J. Kroll, *Z. anorg. Chem.*, 1935, **226**, 23.
6. W. J. Kroll, W. F. Hergert, and L. A. Yerkes, *J. Electrochem. Soc.*, 1950, **97**, 258.
7. E. S. Greiner, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, **188**, 891.
8. H. L. Wain and F. Henderson, *Proc. Phys. Soc.*, 1953, [B], **66**, 515.
9. H. L. Gilbert, H. A. Johansen, and R. G. Nelson, *Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197**, 63.
10. H. B. Goodwin, R. A. Gilbert, C. M. Schwartz, and C. T. Greenidge, *J. Electrochem. Soc.*, 1953, **100**, 152.
11. K. F. Lorking and S. T. Quaass, unpublished work.
12. H. T. Greenaway, S. T. M. Johnstone, and M. K. McQuillan, *J. Inst. Metals*, 1951-52, **80**, 109.
13. H. T. Greenaway, *ibid.*, 1954-55, **83**, (4), 121.
14. C. A. Snively and C. L. Faust, *J. Electrochem. Soc.*, 1950, **97**, 99.
15. J. B. Cohen, *Trans. Electrochem. Soc.*, 1944, **86**, 441.
16. F. Adecock, *J. Iron Steel Inst.*, 1927, **115**, 369.
17. G. A. Geach and D. Summers-Smith, *Metallurgia*, 1950, **42**, 153.
18. R. B. Fischer and J. H. Jackson, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, **188**, 1149.
19. W. J. Kroll, *Z. Metallkunde*, 1936, **28**, 317.
20. H. L. Gilbert, H. A. Johansen, and R. G. Nelson, *U.S. Bur. Mines Rep. Invest. No. 4905*, 1952.
21. British Patent No. 698,425, 1953.

A STUDY OF THE ROOM-TEMPERATURE DUCTILITY OF CHROMIUM *

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With an Appendix on

ANALYTICAL METHODS USED FOR THE DETERMINATION OF NITROGEN
AND OXYGEN IN CHROMIUM

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SYNOPSIS

It has been found possible to produce chromium capable of at least 15% elongation in a room-temperature tensile test. A preliminary examination has been made of some of the factors governing the ductility of this material.

Small amounts of nitrogen, apparently present in solid solution, produce room-temperature brittleness, and embrittlement by this mechanism occurs on heating in air or nitrogen at as low as 650° C. On the other hand, ductility does not appear to be affected by heating in oxygen at these temperatures.

Chromium is notch-sensitive, and surface notches produced by filing or coarse grinding can seriously reduce ductility. This effect can normally be removed by light etching or fine polishing.

Recrystallized chromium can be rendered ductile at room temperature, but is more susceptible to the embrittling factors mentioned above than is the cold-worked material. Thus, a nitrogen content of approximately 0.02 wt.-% (0.07 at.-%) produces brittleness in cold-worked chromium, while <0.001 wt.-% (<0.003 at.-%) appears to be effective in recrystallized material. It is usually necessary to electropolish recrystallized chromium before ductility is achieved.

The temperature-dependence of brittleness in chromium has been confirmed.

A hypothesis, based on Cottrell locking effects, has been proposed to explain these observations.

I.—INTRODUCTION

WORK carried out at the Aeronautical Research Laboratories, Melbourne,^{1,2} has shown that chromium is not inherently brittle at room temperature and has indicated that such brittleness may be associated with an impurity. This appears to be the first time that chromium has been shown to be ductile at room temperature, apart from some tests made in compression by Greiner³ and by Cross.⁴ Earlier work had indicated that, although chromium could be worked at temperatures ranging from 500° to 1250° C., the product was invariably brittle at room temperature.⁵⁻¹¹ These experiments were made on chromium of various purities, and attempts to reduce the impurity content (e.g. reduction of oxygen content by hydrogen treatment) were unsuccessful in producing room-temperature ductility.

Confirmatory evidence on the room-temperature ductility of chromium has since been obtained by other workers. Experiments at the Battelle Memorial Institute¹² have shown that strip produced by rolling arc-melted iodide chromium in air in the temperature range 980°–700° C. failed at 46,000 lb./in.²

in a tensile test and showed no measurable elongation. Such strip could not be bent plastically. However, a more recent private communication from this laboratory indicates that sheet prepared from a more highly refined iodide chromium could be bent plastically at room temperature and even at –25° C., at slow rates of strain. The exact processing details for this material are not known. Another important feature of this work was the attempt made to determine the effect of deliberate additions of oxygen and nitrogen on the plastic behaviour of chromium. A crystal of iodide chromium was heated in each of these gases, strained in compression, and examined microscopically and by X-rays for evidence of deformation. Although the irregular shape of the specimens rendered the results inconclusive, it was of interest that the crystal treated in oxygen showed slip lines after compression, while none were observed after heating in nitrogen. The latter specimen split into several grains during the compression test.

The U.S. Bureau of Mines (Non-ferrous Metals Branch) has recently found some room-temperature ductility in chromium rod, wire, and sheet.¹³ This ductility was achieved only after the removal of a few

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thousandths of an inch of metal surface by chemical or mechanical means.

Sully *et al.*¹⁴ found that sintered chromium showed a sharp transition from brittle to ductile behaviour over a narrow temperature range. This transition temperature varied from 50° to 390° C. according to the material used in preparing the sintered compacts, and was raised by all added elements except oxygen, which had comparatively little effect in concentrations greater than 0.002 wt.-%. The results of some tensile tests made at 20°, 500°, and 900° C. are given in their paper. The ultimate tensile strength decreased from 15,150 to 12,200 lb./in.² and the elongation increased from zero to 4% over this range. These authors were able to deform chromium in compression at room temperature.

As a result of all this work it now seems to be established that chromium is certainly not inherently brittle at room temperature, and there are several indications that brittleness may be produced by an impurity. However, this point has not yet been decided with any degree of certainty, nor has any particular impurity been shown to be effective. Evidence on these and other aspects of the room-temperature brittleness of chromium is presented in the present paper.

II.—PREPARATION OF SPECIMENS

The production details regarding the electrolytic chromium used in this investigation have been reported elsewhere.¹⁵ No metallic impurities were detected spectrographically, and the normal analysis was 0.06 wt.-% (0.19 at.-%) oxygen, 0.005 wt.-% (0.019 at.-%) nitrogen, and less than 0.005 wt.-% (0.022 at.-%) carbon.

In some experiments, chromium of a higher degree of purity was used, produced by modifying the electroplating conditions and by the hydrogen-reduction of as-deposited chromium at 1500° C.¹⁶ The chromium was melted in an argon-arc furnace and forged, swaged, and rolled in mild-steel or mild-steel and stainless-steel sheaths. Details of this practice have already been given.¹

III.—EXPERIMENTAL RESULTS

1. EFFECT OF HEATING CHROMIUM IN AIR, OXYGEN, AND NITROGEN

Previous work¹ has shown that embrittlement of chromium during fabrication can be reduced by taking various precautions to reduce contamination to a minimum. Although not specifically stated in the paper concerned, it appeared that the impurity responsible for brittleness was absorbed from the air space between specimen and sheath. This conclusion has now been checked by observing the effect on bend ductility of heating chromium in air, oxygen, and

nitrogen. In all these experiments, the heat-treatment temperatures were below the recrystallization-temperature range because, as shown later, recrystallization in itself has an influence on ductility. Bend-test specimens were approximately $0.5 \times 0.25 \times 0.03$ in. and were tested in a simple three-point loading device at a strain rate of approximately 0.25 in./min. The specimen rested on two $\frac{1}{8}$ -in.-dia. steel rollers placed $\frac{5}{16}$ in. apart and were bent by a screw-loaded plunger having a $\frac{1}{16}$ -in.-radius cylindrical nose-piece.

For the heating-in-air experiments, small strips of ductile chromium were placed in an alumina boat and heated in an open-ended electric tube furnace in still air. The specimens were removed after the required time, and tested in the as-annealed condition and after the thickness had been reduced various amounts by etching. The results are given in Table I.

TABLE I.—*Effect on Ductility of Heating in Air.*

Treatment in Air	Reduction of Thickness by Etching, in.	Bend Ductility at Room Temperature
560° C. for { 2.5 hr.	Unetched 0.001	Ductile (visible oxide skin removed)
650° C. for { 2 hr.	Unetched 0.002	Brittle Ductile (visible oxide skin removed)
700° C. for { 2 hr.	Unetched 0.0005 0.005 0.019	Brittle " (visible oxide skin removed) " (visible oxide skin removed) Ductile
710° C. for { 6 hr.	Unetched 0.002 0.007 0.011	Brittle " (visible oxide skin removed) " (visible oxide skin removed) 1 piece brittle, 1 piece ductile

These results indicate that chromium is embrittled by heating in air at a temperature as low as 650° C. and that the depth of embrittlement increases with temperature. No conclusion can be drawn regarding the effect of time at temperature. The brittleness of the specimens annealed at 700° C. persists to a much greater depth than can be accounted for by the formation of an oxide skin. Microscopic examination of a cross-section of a strip annealed at 700° C. revealed that the thickness of the oxide layer was only of the order of 0.0001 in.; no nitride was visible in the microstructure nor was there any apparent variation in the number, size, or distribution of oxide particles from surface to interior. There was no evidence of surface cracking or selective grain-boundary penetration of oxide or nitride. No X-ray or microscopic evidence of recrystallization was observed in any of these specimens.

The next step was to determine whether both oxygen and nitrogen embrittled chromium. This was done by heating ductile chromium strip in high-purity nitrogen (oxygen < 20 p.p.m.) and high-purity oxygen (99.65%; impurities not known). All strips were approximately 0.03 in. thick before

treatment. The apparatus used is illustrated in Fig. 1. The specimen was degassed in trichloroethylene and placed in the clear silica tube (E) which had previously been outgassed, and the system was evacuated to 10^{-3} mm. Hg. Gas was introduced and the system flushed and evacuated several times until the nature of the discharge in the discharge tube attached to the system was characteristic of the particular gas being used. These discharges were quite

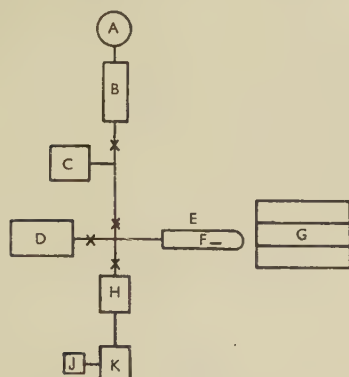


FIG. 1.—Plan Diagram of Gas-Absorption Apparatus.

KEY.

- | | |
|--------------------------|---------------------------------|
| A. Gas. | F. Specimen. |
| B. Drying train. | G. Electric-resistance furnace. |
| C. Gas reservoir. | H. Oil-diffusion pump. |
| D. Philips vacuum gauge. | J. Discharge tube. |
| E. Clear silica tube. | K. Backing pump. |

distinctive, and the presence of residual traces of any unwanted gas was readily detected. The system was evacuated to a pressure of the order of 10^{-5} mm. Hg, and the silica tube containing the specimen was de-

TABLE II.—Effect on Ductility of Heating in Nitrogen or Oxygen.

Treatment	Reduction of Thickness by Etching, in.	Bend Ductility at Room Temperature
45 min. at 700° C. in N ₂	Unetched	Brittle
	0.0005	" (surface film removed)
	0.001	"
	0.002	"
	0.003	"
16 hr. at 700° C. in N ₂	0.004	Ductile
	0.002	Brittle (surface film removed)
	0.005	"
	0.006	Ductile
45 min. at 700° C. in O ₂	0.011	"
	Unetched	Ductile
	0.0005	" (surface film removed)
16 hr. at 700° C. in O ₂	0.002	"
	Unetched	Ductile
	0.002	" (surface film removed)

gassed at 550° C. for 30 min. and cooled. Finally, the system was filled with gas, the specimen tube was isolated and heated as required. All these experi-

ments were carried out at 700° C. for times varying from 30 min. to 16 hr. The results are presented in Table II.

It can be seen that embrittlement of ductile chromium occurs on heating at 700° C. in nitrogen, and that the depth of embrittlement increases with time of annealing. On the other hand, specimens heated under similar conditions in an oxygen atmosphere showed no appreciable embrittlement and were ductile without removing the oxide skin. A further interesting point in this connection is that it was found that chromium could be embrittled by heating for 45 min. at 700° C. in a vacuum of 10^{-2} – 10^{-3} mm. Hg, provided that the residual gas was either air or nitrogen. However, specimens given a similar treatment were ductile without etching, provided that they were outgassed at 550° C. for 30 min. in a high vacuum ($\sim 10^{-5}$ mm. Hg) before heating at 700° C. at a pressure of 10^{-2} – 10^{-3} mm. Hg. The embrittlement in the former case presumably arises largely from nitrogen on the specimen surface being absorbed rather than removed on rapid heating to 700° C.

The fact that the brittleness resulting from heating in nitrogen was due to nitrogen penetration was confirmed analytically on larger specimens, as shown in Table III. These results, in conjunction with those of Table II, indicate that room-temperature brittleness occurs in worked chromium at a nitrogen content of approximately 0.02%.

TABLE III.—Layer Analysis for Nitrogen.

Treatment	Reduction of Thickness by Etching, in.	Nitrogen Content of Layer Removed, wt.-% *
16 hr. at 700° C. in N ₂	0.001	1.40
	0.003	0.20
	0.008	0.017
	0.018	0.008
	Remainder	0.005

* See Appendix (p. 141) for method of nitrogen determination.

A similar satisfactory layer analysis for oxygen could not be made owing to the requirements of the analytical method and the small size of specimen available. However, analyses were made on specimens heated for 16 hr. at 700° C. in oxygen before and after removal of the visible oxide skin, which involved reducing the thickness by approximately 0.001 in. The average values obtained were 0.12 wt.-% oxygen in the first case, as compared with 0.05 wt.-% oxygen (which was the oxygen content of the material before treatment) in the second case. These experiments, although not completely satisfactory, do suggest that oxygen penetration does not occur to any appreciable extent during the treatment described above.

Of interest to later work is the fact that specimens heated in nitrogen for 16 hr. at 700° C. were brittle

after a reduction in thickness of 0.004 in. by electro-polishing.

2. EFFECT OF SURFACE CONDITION ON DUCTILITY

During attempts to produce tensile specimens from rolled chromium strip by grinding the surface flat and parallel and by filing to shape, it was found that cracking frequently occurred even though the strips had originally shown considerable bend ductility. The fractured pieces of such a specimen could not be deformed plastically at room temperature, but bend ductility was restored by polishing with 600-grade abrasive paper or by etching 0.001–0.002 in. from the surface.

The effects of such surface treatments on the tensile properties of chromium at room temperature are shown in Table IV. Details of the testing and electropolishing procedures have been given elsewhere.¹

TABLE IV.—*Effect of Surface Treatment on Tensile Properties.*

All specimens rolled at 600° C.

Surface Condition	Surface Hardness, D.P.N., (5-kg. load)	0.2% Proof Stress, lb./in. ²	Max. Stress, lb./in. ²	Elongation, % on 0.5 in.
Ground and filed .	208	...	89,000	0
Acid etched .	202	45,500	78,500	11
Electropolished .	190	55,000	74,500	15

Microscopic and X-ray examinations were made on the surfaces of ductile chromium specimens which had been, respectively, filed, filed and polished on 600-grade abrasive paper, and filed and etched to a depth of 0.001–0.002 in. Microscopic examination of taper sections of a filed surface revealed the presence of a thin surface layer which appeared to be more heavily cold worked than the bulk of the specimen. This feature was absent in specimens subsequently etched or polished with fine abrasive paper. X-ray back-reflection photographs showed that the Debye-Scherrer rings were diffuse when the specimen surface had been filed, but became sharp when the surface was etched or finished with fine paper. No evidence of recrystallization in the surface layers could be detected.

3. EFFECT OF RECRYSTALLIZATION

In the results presented above, consideration has been given only to ductility in chromium rolled in the temperature range 600°–900° C., which produces a cold-worked material with an elongated grain structure, although X-ray examination shows that a preferred orientation is not normally developed. It had previously been reported² that rolled chromium,

which had been recrystallized, could be rendered ductile at room temperature, although in this case it was necessary to reduce the thickness of the strip further by etching than was found necessary for cold-rolled material. However, in those experiments, the extent of recrystallization was judged from the microstructure, and subsequent X-ray studies have shown that some residual cold work may remain on annealing cold-worked chromium, even though the microstructure appears to consist solely of equiaxed grains. This fact is illustrated by photomicrographs and X-ray back-reflection photographs (Figs. 2–5, Plates XXIII and XXIV) taken on chromium sheath-rolled at 560° C. and then annealed at temperatures in the range 600°–950° C. The full results are presented in Table V.

TABLE V.—*Recrystallization Texture of Rolled and Annealed Chromium.*

Annealing Treatment	Hardness, D.P.N. (5-kg. load)	Microstructure	X-Ray Back-Reflection Photograph
As rolled at 560° C.	260	Elongated grain structure	Diffuse rings
2 hr. at 600° C.	232	Elongated grain structure	Sharp rings
2 hr. at 700° C.	227	Elongated grain structure	Sharp rings
2 hr. at 750° C.	216	Elongated grain structure	Sharp rings together with a few sharp spots
2 hr. at 800° C.	193	Grain growth beginning from fine-grained regions	Sharp rings and spots
2 hr. at 850° C.	157	Equiaxed grain structure	Faint rings and many sharp spots
2 hr. at 900° C.	138	Equiaxed grain structure	Sharp spots

Chromium rolled at 560° C. had a distinctly banded microstructure consisting of areas of fine-grained and coarse-grained material (see Fig. 2 (b)), and all grains were elongated in the rolling direction. No marked change in microstructure occurred on heating until a temperature of approximately 800° C. was reached, when recrystallization began in the fine-grained areas (see Fig. 3 (b)) and appeared to be complete after 2 hr. at 850° C. Corresponding changes in the X-ray photographs took place on heating, with two exceptions. Sharp spots from recrystallized grains were observed at a lower temperature than that at which microscopical evidence of recrystallization could be obtained (cf. Figs. 3 (a) and 3 (b)), and X-ray photographs were more sensitive to residual deformation in the partially recrystallized structure than was the microscope (cf. Figs. 4 (a) and 4 (b)). The sharpening of the Debye-Scherrer rings and the decrease in

hardness observed on heating to 600° C. were presumably due to recovery.

The effect of recrystallization on room-temperature ductility is illustrated in Fig. 7. Hardness and bend tests were made, and X-ray photographs taken, on chromium samples rolled at 600° C. to a thickness of approximately 0.06 in. and annealed in their sheaths at various temperatures in the range 700°–950° C. After removal from the sheath, each rolled strip was etched to a thickness of approximately 0.035 in. to remove any contaminated material and then slit

4. DUCTILITY OF COMPLETELY RECRYSTALLIZED CHROMIUM

The results in the previous section show that chromium strip, rolled in the normal way and annealed to produce a completely recrystallized structure, is brittle irrespective of whether the surface is acid etched or electropolished. However, specimens of recrystallized chromium have been produced which showed some bend ductility at room temperature, and this has been achieved by iron plating the chromium

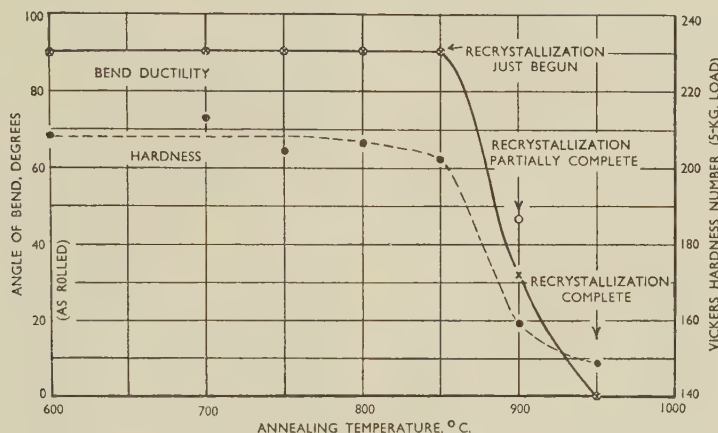


Fig. 7.—Effect of Recrystallization on Room-Temperature Ductility.

KEY.

○ Bend tests on electropolished specimen.

× Bend tests on etched specimen.

● Vickers Diamond Pyramid Hardness.

Note: Specimens heated to a temperature not exceeding 850° C. bend through 90° on the machine, as shown. They were all subsequently bent through 180° without fracture.

longitudinally to form bend specimens. In all cases, one of these specimens was chemically etched and the other electrolytically polished to a thickness of 0.03 in. Thus, the size of the bend specimens used was approximately $1 \times 0.125 \times 0.03$ in. and bend tests were made in the three-point loading machine previously described.

As shown in Fig. 7, the specimens annealed at temperatures up to 850° C. could be bent through 180° without fracture, and at this temperature recrystallization was just beginning, as was indicated by X-ray photographs and hardness measurements. (It will be noted that recrystallization set in at a higher temperature in these experiments as compared with those reported in Table V; this was possibly due to the slightly higher rolling temperature used.) The specimens heated to 900° C., in which recrystallization was well advanced (X-ray photograph corresponding to Fig. 4 (a)), deformed plastically by a small amount before fracture, a slightly greater amount of deformation being observed in the electropolished specimen. The fully recrystallized specimens fractured in a completely brittle manner.

to reduce to a minimum impurity pick-up during fabrication. This material was ductile when electropolished but brittle when chemically etched.

It has also been shown¹ that electrolytic chromium purified by hydrogen treatment at 1500° C., which has an equiaxed structure, exhibited considerable room-temperature ductility in both the electropolished and chemically etched conditions. The influence of purity was emphasized by the fact that similar material, which had become accidentally contaminated during the hydrogen treatment, was brittle even after electropolishing. These experiments are summarized in Table VI.

Some preliminary experiments have revealed another interesting feature, viz. that recrystallized chromium, normally brittle at room temperature, becomes extremely ductile at 100° C. or even lower. Furthermore, if this material is slightly deformed at such temperatures, it then becomes possible for considerable additional deformation to be carried out at room temperature. Parts of the same specimen not deformed at these slightly elevated temperatures remain brittle at room temperature. After this treat-

ment, X-ray photographs of the deformed area show some blurring of the spots from the recrystallized grains (see Fig. 6, Plate XXIV).

TABLE VI.—*Effect of Purity on Ductility of Recrystallized Chromium.*

Method of Preparation	Nitrogen Content	Surface Condition	Room-Temperature Ductility
Iron plated, rolled at 850° C., annealed at 950° C. for 45 min.	Not detected	Etched Electro-polished	Brittle Ductile
As deposited, hydrogen-treated at 1500° C.	Not detected		Ductile "
As deposited, hydrogen-treated at 1500° C., accidentally contaminated with air	0.035 wt.-%	Electro-polished	Brittle

IV.—DISCUSSION

1. FACTORS INFLUENCING ROOM-TEMPERATURE DUCTILITY

The first important point arising from these experiments is the fact that chromium can be produced which shows considerable room-temperature ductility in tension and bending. The tensile results quoted were of necessity obtained on quite small specimens, which were thus geometrically unfavourable to the attainment of high elongation values, and it is likely that considerably greater ductility will be shown in the same material when it becomes possible to increase the specimen size. However, even the amount of ductility so far revealed considerably enhances the prospects of producing a chromium-base alloy having useful high-temperature properties and yet showing a certain amount of room-temperature ductility.

The second point of interest concerns the factors producing brittleness in chromium. It can be seen that there is a considerable amount of evidence indicating that chromium can be embrittled either by nitrogen in solution or by stress concentrators at the surface.

Experiments on argon-sealed billets and on billets copper plated or iron plated before sheathing¹ provide considerable circumstantial evidence that chromium can be rendered brittle by an impurity absorbed from the air. This was confirmed directly by embrittling ductile chromium by heating in air below the recrystallization temperature, and there were several features of interest about these latter experiments. In the first place, the brittleness extended to a much greater depth than did the surface oxide film, and there was no microscopical evidence of surface cracking or accumulation of oxide or nitride particles in the surface layers. Secondly, X-ray examination failed to reveal any change in lattice

parameter, or the presence of any additional phase, in chromium embrittled by heating in air once the oxide skin had been removed.

Attempts were next made to distinguish between nitrogen and oxygen as embrittling agents by heating ductile chromium in these gases. It was found that nitrogen produced brittleness, while oxygen did not. Increasing the time of heating in nitrogen resulted in a greater depth of embrittlement, and nitrogen appeared to be effective in extremely small amounts, e.g. of the order of 0.02 wt.-% for cold-rolled chromium. Since microscopic examination again failed to reveal any nitride particles in the outer layers of chromium so treated, it is assumed that the nitrogen was entirely in solid solution. The situation as regards oxygen is not so clear, since the experiments were not sufficiently sensitive to determine whether significant oxygen penetration occurred. The conclusion from these experiments is, therefore, that room-temperature brittleness can be produced in chromium by nitrogen in solution.

Evidence in the present work for the embrittlement of chromium arising from surface condition is twofold. In the first place, brittleness has been found in both tensile- and bend-test specimens of rolled chromium in which the surface had been filed or finished on a grinding wheel. This brittleness disappeared if the specimens were ground with fine abrasive paper or lightly etched. In this connection it should be mentioned that investigators at the U.S. Bureau of Mines¹⁷ have found a similar embrittlement to occur in ductile chromium during wire drawing at 350° C., and it was also shown that this brittleness could be removed by etching the wire surface. The second point involving surface condition was the necessity, in general, to electropolish recrystallized specimens, which seemed to be less ductile than cold-rolled strip, as discussed later, before ductility was achieved. Also, ductile electropolished specimens of recrystallized chromium could usually be made brittle by light etching.

The question arises as to whether the two embrittling agencies mentioned above are really separate effects or whether they can be explained by a single cause. For example, it could be held that the embrittlement produced by heating in nitrogen is the result of the formation of fine surface cracks by nitrogen absorption. These would act as stress concentrators, causing brittle failure, and would be removed by etching. However, this does not appear to be so, because no such cracks have been observed even in specimens which had been embrittled to a considerable depth by nitrogen absorption. Also, although crack formation by gases is found in chromium and other metals, it always seems to involve the formation and diffusion of atomic hydrogen. Since the hydrogen atom is much smaller than the nitrogen molecule, and since embrittlement of this type seems to depend largely on the relative sizes of the gas and metal atoms, it appears unlikely that nitrogen would cause cracking in this way. On the

other hand, it is known that filing the surface of metals in air can lead to the formation of surface oxide, presumably as a result of the high local temperatures developed. Hence it seems possible, in principle, that the brittleness induced in chromium by filing or grinding could be caused by pick-up of nitrogen and not by the formation of surface stress concentrators. However, once again this seems unlikely because, as shown in Table VI, brittleness can be induced in recrystallized, electropolished chromium merely by light etching, where nitrogen absorption would appear to be out of the question.

A third feature of this work is the fact (see Fig. 7) that cold-worked chromium normally becomes less ductile as recrystallization proceeds, a phenomenon previously observed in molybdenum¹⁸ and tungsten.¹⁹ The specimens in this series were all prepared from the same swaged rod, so that the nitrogen content would not be expected to vary appreciably from specimen to specimen, and each specimen was electropolished. If the brittleness of these specimens is due to nitrogen, it appears that the minimum nitrogen content to produce brittleness in recrystallized material is much less than for cold-worked specimens. This is confirmed by the results given in Table VI, where it is shown that the change from ductile to brittle behaviour in two electropolished, equiaxed specimens occurred at a nitrogen content below the limit of chemical analysis (<0.001 wt.-%). On the other hand, this change occurred for a cold-worked chromium sample at a nitrogen content of the order of 0.02 wt.-% (see Tables II and III).

2. BRITTLINESS AND COTTRELL LOCKING

Any explanation of the brittleness of chromium must account for the following four facts:

(a) Brittleness can be produced by very small amounts of nitrogen in solid solution.

(b) Recrystallized chromium is more susceptible to embrittling factors than the cold-worked material.

(c) Brittleness is temperature-dependent, i.e. even material which is brittle at room temperature can be deformed plastically at slightly elevated temperatures.

(d) Chromium is notch-sensitive.

It is found that brittle fracture in chromium is almost invariably transcrystalline, so that it does not appear that brittleness due to nitrogen is the result of the formation of grain-boundary nitride films. Additional evidence is that no grain-boundary films have been observed microscopically nor any nitride particles which could have acted as stress concentrators leading to brittle fracture. Tungsten has been shown to be ductile in the form of single crystals or in the form of drawn wire having a high degree of pre-

ferred orientation, but to be brittle when it has an equiaxed recrystallized grain structure.¹⁹ This has been ascribed to the fact that a heavily cold-worked tungsten wire consists essentially of a "bundle" of single crystals whose orientation is favourable to slip, and this structure is, of course, destroyed by recrystallization. Such an explanation is hardly applicable to chromium since: (i) the cold-rolled chromium strip used in this investigation has not been found to have a marked preferred orientation, and (ii) both cold-rolled and recrystallized chromium have been produced in ductile and brittle conditions at room temperature.

The most promising explanation of the behaviour of chromium is one based on "Cottrell locking" effects. It is now well established that yield points in metals are due to trace impurity elements which affect the properties of dislocations in the metal.* In at least one such system, i.e. iron containing carbon and nitrogen in solid solution,²¹ it appears that there is a relationship between the yield-point phenomenon and behaviour at low temperatures. Single crystals of iron showed considerable elongation at liquid-air temperatures, provided that the specimens were in a condition in which they would not have shown a yield point at room temperature (i.e. were overstrained or treated to remove nitrogen and carbon). However, if the crystals contained carbon and nitrogen and were in the strain-aged condition (i.e. would have shown a yield point), they deformed at liquid-air temperatures by twinning instead of by slipping and the total elongation was small. This behaviour has been explained by the fact that, in the strain-aged specimen, the stress for slip at liquid-air temperatures was raised above that for twinning owing to the large temperature-dependence of slip in yield-point systems. Such an argument is also likely to be applicable to fracture stress, so that one would expect that Cottrell locking would have a considerable influence on the transition from brittle to ductile behaviour as the testing temperature is varied. Experimental verification of this point is most desirable.

An explanation of the room-temperature brittleness of chromium can be given along these lines. It is postulated that the presence of nitrogen in solid solution in chromium makes it possible for the Cottrell locking mechanism to operate, and that chromium in which the dislocations are anchored by nitrogen atoms exhibits similar behaviour at room temperature to that shown by iron containing carbon and nitrogen at sub-zero temperatures. This would require the combining force between nitrogen atoms and dislocations in chromium to be stronger than that between dislocations and carbon and nitrogen atoms in iron. No information is available on this point. If the nitrogen content is reduced below a critical concentration with respect to the dislocation density, significant Cottrell locking does not occur and the material is ductile. Also, increasing the temperature

* For a review of this subject, see A. H. Cottrell.²⁰

provides thermal energy which reduces the effectiveness with which dislocations are anchored by nitrogen atoms, so that a temperature is reached at which dislocation locking is ineffective and the material becomes ductile. A similar disappearance of the yield-point phenomenon is known to occur as the testing temperature is increased.

A theory such as this could explain the fact that it was found more difficult to produce ductility in recrystallized than in cold-worked chromium. Annealing for recrystallization would provide a greater opportunity for diffusion of impurity atoms to dislocations, and, perhaps more significantly, would reduce the dislocation density, so that a smaller number of nitrogen atoms would be required to form atmospheres of a given concentration around the dislocations in an annealed as compared to a cold-worked material. Examination of a simple model shows that the impurity concentration for complete locking falls from 0.1 to 0.00001 at.-% as a heavily cold-worked material is annealed.²² This is to be compared with the change from room-temperature ductility to brittleness at nitrogen contents of approximately 0.02 wt.-% (0.07 at.-%) and <0.001 wt.-% (<0.004 at.-%) for cold-worked and recrystallized chromium, respectively. The converse effect has been observed in zinc single crystals in which yield points are produced by nitrogen in solution. In this case it was found that, for a given nitrogen content, increasing the dislocation density by plastic deformation produced a progressive decrease in yield-point value until ultimately no yield point was observed.²³ This theory also explains why initially brittle, recrystallized chromium becomes ductile at room temperature after a small amount of deformation at a slightly elevated temperature (100° C.), since such deformation would be expected to remove the dislocations from their solute atmospheres. The fact that final room-temperature ductility is confined to those areas deformed at 100° C. follows automatically.

It is obvious that this explanation of the mechanism by which nitrogen produces brittleness in chromium can at present be put forward only tentatively, and no complete solution is likely until a great deal more information is available on the constitution and activities of dilute solutions of metals and gases in chromium, and on the general relationship between Cottrell locking and brittleness. For example, it is likely that the form, as well as the amount, of certain impurities in chromium will have an important influence on brittleness (cf. the work of Cottrell and Leak²⁴ on the effect of the distribution of carbon and nitrogen on strain-ageing in iron). However, it would be of great practical and theoretical interest to determine the effect of nitrogen, and other possible embrittling impurities, on the mechanical properties of chromium, particularly on the transition from brittle to ductile failure, and such a programme is in progress

in the authors' laboratories. Further improvement in the ductility of chromium will also be attempted by additional purification of the starting material, or by rendering impurities ineffective as regards brittleness by experimental additions or heat-treatments.

The explanation of the other agency found to induce brittleness in chromium, viz. surface notches or pits, appears to be self-evident, since triaxial stresses at the root of a notch are known to raise the effective yield stress.²⁵ Hence, in a notched specimen, one would anticipate brittle behaviour when the effective yield stress is increased to such a value, through the agency of notches and Cottrell locking, that it exceeds the fracture stress. This would perhaps explain why recrystallized chromium is more susceptible to the effect of surface notches than is similar cold-worked material. It may seem strange at first sight that a material showing reasonable ductility in a tensile or bend test should be notch sensitive to this extent. However, it has been shown that there is no direct correlation between notch sensitivity and tensile elongation, as is well illustrated by the comparatively high notch sensitivity of copper.*

3. COMPARISON WITH OTHER RESULTS

Finally, it is of interest to consider the previous work on the brittleness of chromium from the point of view of the experiments now described. Workers at the U.S. Bureau of Mines¹¹ have reported zero room-temperature ductility in hydrogen-reduced chromium containing 0.03 wt.-% nitrogen. Such a result would be expected from the present work. These workers have subsequently stated that brittleness may be induced during wire drawing and that such brittleness can be removed by surface etching;¹⁷ this is presumably analogous to the present authors' effect of surface notches. The Battelle Institute workers¹² have failed to show room-temperature ductility in tension or bending in "iodide" chromium in which the nitrogen content was initially 0.013 wt.-%. However, room-temperature ductility has been achieved in material of higher purity, but the analysis and fabrication details are not known. It may be significant that these investigators produced evidence of deformation at room temperature in an "iodide" chromium crystal after heating in oxygen, but not after heating in nitrogen. It is not surprising that Sully and his co-workers failed to produce any room-temperature ductility in sintered chromium specimens.¹⁴ The materials used had a high nitrogen content (0.02–0.04 wt.-%), they had been recrystallized during sintering, and they contained stress concentrators in the form of residual porosity. The present work shows that all these influences militate against room-temperature ductility.

* For a review of this subject see M. S. Paterson.²⁶

V.—CONCLUSIONS

(1) Chromium has been produced which shows sufficient ductility in tension and bending at room temperature to indicate that the production of ductile chromium-base alloys for use at high temperatures is a definite possibility.

(2) Nitrogen in small amounts, probably in solid solution, has been shown to produce room-temperature brittleness in chromium. Oxygen does not appear to be effective in this regard.

(3) The chromium used in this work appears to be notch sensitive.

(4) Cold-worked chromium normally becomes less ductile as recrystallization proceeds.

(5) Completely recrystallized chromium has been made ductile at room temperature, but is more susceptible to embrittling agencies than is the cold-worked material.

(6) The temperature-dependence of brittleness in chromium has been confirmed.

ACKNOWLEDGEMENTS

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APPENDIX

ANALYTICAL METHODS USED FOR THE DETERMINATION OF NITROGEN AND OXYGEN IN CHROMIUM

By E. J. Lumley

The method used at the Aeronautical Research Laboratories for the estimation of nitrogen in chromium is a modification of the well-known Allen distillation method able to handle the small samples generally available. The pulverized sample (usually 0.5 g.) is dissolved in dilute sulphuric acid. Undecomposed nitrides are collected in a precipitate of barium sulphate (formed by the addition of barium chloride to the solution), and, after centrifuging and

decanting, are decomposed by boiling with a sulphuric acid-potassium sulphate mixture. The combined solutions are then subjected to a normal sodium hydroxide distillation in a semi-micro unit which has been freed from ammonia by a preliminary distillation. The distillate is Nesslerized, allowed to stand for a fixed time, and the absorption measured in a Spekker absorptiometer, using 2-cm. cells, Ilford Spectrum Violet filters No. 601, and a water setting of 1.0. Results are referred to a calibration graph prepared by distilling a series of varying amounts of a solution of A.R. ammonium chloride. A blank is carried out on all reagents and procedures.

Nesslerization as a means of detecting ammonia is very sensitive. Hence all reagents used are carefully measured or weighed, ammonia-free water is used where necessary, all operations are strictly standardized, and the procedure is carried out in an ammonia-free atmosphere.

Under ideal conditions the absorptiometer is capable of differentiating (and estimating) 2×10^{-6} g. of nitrogen, with good reproducibility. With a sample of 0.5 g. of chromium, and a reported nitrogen content of 0.001 wt.-%, this is equivalent to a probable error of $\pm 0.0004\%$ (or approximately 40% error), and with a reported nitrogen content of 0.01 wt.-% to an error of approximately 4%. Higher nitrogen values are probably accurate to the normal absorptiometric value, i.e. $\pm 1\%$. Sufficient experiments to justify a precise statement of accuracy have not yet been carried out. In addition, the method itself is, at present, open to some suspicion, in that there is no conclusive evidence available to indicate whether uncombined nitrogen (i.e. molecular or atomic nitrogen dissolved in the chromium) is estimated together with the combined nitrogen, and further comparison with the results of vacuum-fusion analysis is required. However, it is known that the results obtained by the acid digestion-distillation method and the vacuum-fusion method agree well for the determination of nitrogen in molybdenum²⁷ and titanium.²⁸

Oxygen determinations were made by the normal acid solution method. The chromium specimen is vacuum-heated for 1 hr. at 850°C. to convert the oxygen present to Cr_2O_3 . A pulverized 1-g. sample is dissolved in hot 10% hydrochloric acid, allowed to stand cold for 2 hr., then filtered through a close paper (Whatman 42) and washed with cold 4% hydrochloric acid. Finally, the residue of Cr_2O_3 is ignited and weighed, and the result calculated to oxygen.

REFERENCES

1. F. Henderson, S. T. Quaass, and H. L. Wain, *J. Inst. Metals*, 1953-54, **83**, (4), 126.
2. H. L. Wain and F. Henderson, *Proc. Phys. Soc.*, 1953, [B], **66**, 515.
3. E. S. Greiner, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, **188**, 891.
4. H. Cross, *Iron Steel Inst. Special Rep.*, 1952 (**43**), 346 (discussion).
5. M. A. Hunter and A. Jones, *Trans. Amer. Electrochem. Soc.*, 1923, **44**, 23.
6. J. W. Marden and M. N. Rich, U.S. Patent No. **1,750,367**, 1930.
7. W. J. Kroll, *Z. anorg. Chem.*, 1935, **226**, 23.
8. W. J. Kroll, W. F. Hergert, and L. A. Yerkes, *J. Electrochem. Soc.*, 1950, **97**, 258.
9. F. Adcock, *J. Iron Steel Inst.*, 1927, **115**, 369.

10. A. Brenner, P. Burkhead, and C. W. Jennings, *J. Research Nat. Bur. Stand.*, 1948, **40**, 31.
11. H. L. Gilbert, H. A. Johansen, and R. G. Nelson, *Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197**, 63.
12. H. B. Goodwin, R. A. Gilbert, C. M. Schwartz, and C. T. Greenidge, *J. Electrochem. Soc.*, 1953, **100**, 152.
13. H. L. Gilbert and H. A. Johansen, *Iron Age*, 1954, **173**, (3), 93.
14. A. H. Sully, E. A. Brandes, and K. W. Mitchell, *J. Inst. Metals*, 1952-53, **81**, 585.
15. H. T. Greenaway, S. T. M. Johnstone, and M. K. McQuillan, *ibid.*, 1951-52, **80**, 109.
16. H. T. Greenaway, *ibid.*, 1953-54, **83**, 121.
17. H. L. Gilbert, private communication.
18. R. A. Long, K. C. Dike, and H. R. Bear, *Metal Progress*, 1951, **60**, 81.
19. C. J. Smithells, "Tungsten", 3rd edition. 1952: London (Chapman and Hall).
20. A. H. Cottrell, "Progress in Metal Physics", edited by B. Chalmers, Vol. IV, Chapter 5. 1953: London (Pergamon Press).
21. A. T. Churchman and A. H. Cottrell, *Nature*, 1951, **167**, 943.
22. A. H. Cottrell, "Progress in Metal Physics", edited by B. Chalmers, Vol. I, p. 96. 1949: London (Butterworths Scientific Publications).
23. H. L. Wain, *Proc. Phys. Soc.*, 1952, [B], **65**, 886.
24. A. H. Cottrell and G. M. Leak, *J. Iron Steel Inst.*, 1952, **172**, 301.
25. E. Orowan, *Rep. Progress Physics*, 1948-49, **12**, 185.
26. M. S. Paterson, *Symposium on Failure of Metals by Fatigue, Univ. Melbourne*, 1946, 309.
27. M. W. Mallett and C. B. Griffith, *Trans. Amer. Soc. Metals*, 1954, **46**, 375.
28. N. P. Allen, private communication.

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SYNOPSIS

A redetermination has been made of the surface tension of sodium, and its temperature coefficient has been established over the range 98°–450° C. The maximum-bubble-pressure method of measurement was employed.

The surface tension at the melting point, relative to an argon atmosphere, is 190.8 dynes/cm. and the temperature coefficient over the range studied is -0.1 dyne/cm./°C. The presence of an oxide film on the sodium surface increases the surface tension, and this effect may account for the discrepancy between the present and previous data.

The surface-tension values are in keeping with several empirical relationships existing between this property and other physical constants of liquid metals. A comparison of the values obtained by experiment with those calculated theoretically does nothing to substantiate the validity of the former owing to the uncertainty in the latter; likewise the experimental result does not indicate which theoretical treatment is the most accurate.

I.—INTRODUCTION

THE surface tension of sodium is of interest in both practical and theoretical metallurgy. Thus, in the practical application of sodium as a high-temperature coolant, a factor affecting the heat-transfer characteristics of the system is the ease with which the sodium wets the heat-exchange tubes. The researches of Bailey and Watkins¹ have established the significance of surface tension in regard to the wetting of solid by liquid metals. In the related problem of the corrosion of solids by liquid metals, similar factors may be important in determining the rate and extent of attack. In theoretical metallurgy, a number of physico-mathematical calculations of the surface energy of metals have been made, especially for the alkali metals, for which the Sommerfeld free-electron model of metallic structure is approximately true. The final verification of these calculations depends upon the existence of accurate experimental data.

Poindexter and Kernaghan² have reported values for the surface tension of sodium and its temperature coefficient, but a redetermination of these properties seemed desirable for the following reasons. The sessile-drop method which they employed is very sensitive to surface contamination. This is especially so in the case of sodium, in which the solubility of oxide is extremely low³ and which is chemically reactive. Moreover, the reported measurements were made *in vacuo* over a restricted temperature range; for the interfacial-tension studies now envisaged, values against argon were required up to 450°–500° C.

II.—METHODS OF MEASURING SURFACE TENSION

1. SELECTION OF EXPERIMENTAL TECHNIQUE

The surface tension of liquids may be measured by either static or dynamic methods. The latter present

certain practical difficulties when applied to liquid sodium, and moreover, since the surface-tension values when obtained were to be applied to a case where the sodium surface would be stationary, only static methods of measurement were considered. The following methods were possible:

- | | |
|--------------------|-----------------------------|
| (a) Capillary-rise | (d) Drop-volume |
| (b) Detachment | (e) Pendant-drop |
| (c) Sessile-drop | (f) Maximum-bubble-pressure |

An overriding consideration in selecting a method was that measurements had to be made up to 500° C. with a minimum of contamination of the sodium. Experience indicated that, with the possible exception of certain refractory oxides, the only materials capable of resisting attack at this temperature were metals of the transition group, and the use of an all-metal apparatus imposed certain restrictions on the method adopted.

Methods (a) and (b) require an exact knowledge of the contact angle formed by the liquid on the capillary or plate material. As this information was lacking for sodium, these methods were rejected. Method (c) had been employed by Poindexter and Kernaghan², and the selection of an alternative procedure therefore seemed desirable. Furthermore, in the sessile-drop method, surface contamination has a pronounced and possibly permanent effect on the surface tension of sodium. A similar criticism is applicable to methods (d) and (e) and made their use in conjunction with this element undesirable.

The maximum-bubble-pressure method has distinct advantages for measurements on sodium. Each successive measurement is made on a freshly formed surface, so that surface-contamination effects are reduced to a minimum. The method may be carried out remotely, no visual measurements being necessary at or near the liquid surface. Finally, the mechanics

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of the bubble formation and detachment have been thoroughly investigated, and an exact method has been established for obtaining absolute surface-tension figures from the experimental data.

2. THE MAXIMUM-BUBBLE-PRESSURE METHOD

One component of the maximum pressure required to form and detach a gas bubble from an orifice immersed in a liquid is due to surface tension, and may be used in conjunction with a knowledge of the curvature of the bubble to determine this property. Thus, when the bubble is small enough to be taken as spherical, the relationship may be expressed as:

$$P_{max.} = P_h + P_{s.t.} \\ = gh(\rho - \rho_0) + \frac{2\sigma}{r} \quad (1)$$

where $P_{max.}$ = maximum pressure.

P_h = component of $P_{max.}$ due to the head of liquid above the orifice.

$P_{s.t.}$ = component of $P_{max.}$ due to the liquid surface tension.

g = gravitational constant.

h = head of liquid above the orifice.

ρ = liquid density.

ρ_0 = gas density.

σ = surface tension of the liquid.

r = orifice radius.

In the application of equation (1), two factors have to be considered. It must be ascertained whether the r involved is the external, internal, or some intermediate radius of the orifice, and under conditions where the postulate of a spherical bubble is not applicable, a correction must be applied for the effect of gravitational distortion of the bubble curvature.

Porter⁴ has analysed the mechanism of bubble

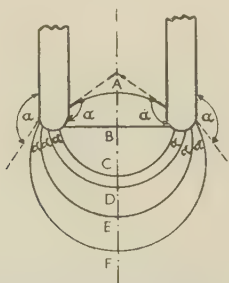


Fig. 1.—Illustrating Stages in Bubble Formation at the Orifice.

formation. Applying the Poisson-Rayleigh equation to the liquid meniscus as the bubble is formed, he calculated the pressure required to extend the meniscus through the several stages from the internal to the external radius of the orifice (Fig. 1), the only condition applied being that the contact angle α of the liquid on the orifice material shall have the equilibrium value at all times. Thus, it is shown that the equilibrium pressure may have a maximum value at either position C or position E (Fig. 1), depending upon the

particular values of internal and external radius and contact angle applicable in any given case; the contact angles considered fall in the range 90° – 150° . The final analysis leads to a graphical relationship between the surface-tension component of the pressure, $P_{s.t.}$, and the orifice radius, r , from which it may be deduced whether the internal or external radius is operative in a given case. Fig. 2 gives this relationship where both parameters are in reduced units, i.e. cm./ β , where:

$$\beta^2 = \sigma/g(\rho - \rho_0) \quad (2)$$

This relationship is employed by finding the value of $P_{s.t.}$ corresponding to the particular internal radius

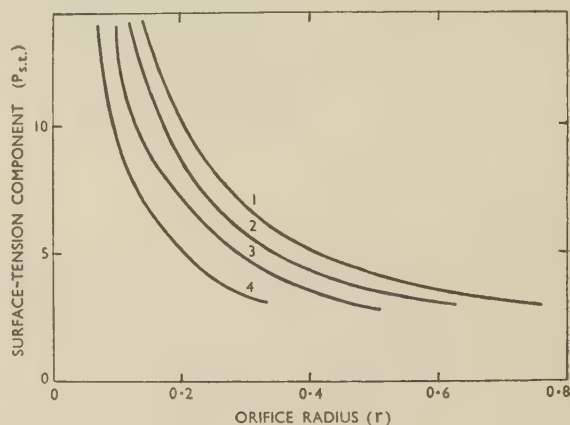


Fig. 2.—Porter's⁴ Pressure/Radius Relationship.

Curve No.	Contact Angle
1	90°
2	120°
3	135°
4	150°

being used, on the specific contact-angle curve appropriate to the system under investigation; the value of $P_{s.t.}$ for the external radius is read off the 90° curve. The greater of these two values indicates which radius corresponds to the development of maximum bubble pressure with a given combination of orifice dimensions and contact angle. This procedure was employed in selecting an orifice suitable for measurements on sodium, the assumption being made that the contact angle of sodium on stainless steel, the material of the orifice tube, was greater than 90° . The orifice finally selected was such that the external radius corresponded to the point of maximum bubble pressure.

Two methods have been proposed for correcting experimental data to give absolute surface-tension figures. The first, proposed by Schrödinger,⁵ makes use of the formula:

$$\beta^2 = \frac{rP_{s.t.}}{2} \left(1 - \frac{2}{3} \cdot \frac{r}{P_{s.t.}} - \frac{1}{6} \cdot \frac{r^2}{P_{s.t.}^2} \right) \quad (3)$$

Expression (3) is accurate only for small values of $(r/P_{s.t.})$, and while the limits of application of the formula have not been clearly defined, its use in the present case seemed unwise; the low order of magnitude of the surface tension of sodium ensures

that $P_{s.t.}$ will be small and the ratio $(r/P_{s.t.})$ correspondingly large. The second method, developed by Sugden⁶ is valid over a wide range of orifice diameters, as it is derived from the fundamental equation relating pressure difference across a liquid meniscus to surface tension; the solution of this equation for conditions appropriate to the maximum-bubble-pressure method is outlined in Appendix I (p. 151). In this way, the function β^2 (see equation (2)) is related to $P_{s.t.}$, the surface-tension component of the maximum pressure, thus:

$$\beta^2 = X \cdot P_{s.t.}/2 \quad (4)$$

The factor X is related to the function $(r/\sqrt{2} \cdot \beta)$, and Sugden gives tables from which values of X can be determined. This correction has been applied to all the experimental results of the present study.

III.—EXPERIMENTAL

1. APPARATUS

A diagrammatic sketch of the apparatus is shown in Fig. 3. A stainless-steel crucible (*B*) contained

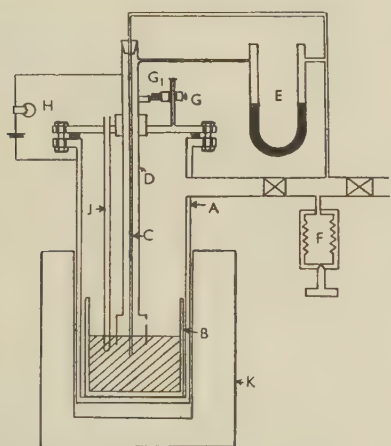


FIG. 3.—Surface-Tension Apparatus (Diagrammatic).

KEY.

A. Outer vessel.	F. Bellows system.
B. Crucible.	G, G ₁ . Levelling arms.
C. Orifice tube.	H. Electrical circuit.
D. Manometer tube.	J. Thermocouple sheath.
E. Manometer.	

the 250-c.c. sodium sample and was totally enclosed by an outer vessel (*A*) of similar material. The orifice tube (*C*) was likewise of stainless steel. The tip of this tube had previously been given a fine finish by metallographic polishing, at right angles to the longitudinal axis, with the tube mounted in Wood's metal. The external diameter of the orifice was 0.141 cm., and this dimension was used as the effective orifice radius; the measurement of the orifice tip was carried out optically. Coaxial with the orifice tube was a second tube (*D*), which transmitted the pressure at the sodium surface to the second limb of the manometer; fixed relative to one another, tubes (*C*) and (*D*) could be adjusted vertically via a Wilson

vacuum seal in the cover-plate of (*A*). Tube (*D*) had an enlarged end-piece which dipped below the sodium surface during a determination; a small hole in this enlarged section provided a connection between the main atmosphere and the manometer. This design was adopted in an attempt to reduce the pulsing of the manometer levels, which became noticeable at higher temperatures, an effect referred to later.

The manometer (*E*) was of conventional design, except that the limb communicating with the atmosphere of the vessel was of larger diameter (2.9 cm.) than the orifice limb (0.6 cm.); this arrangement was also designed to minimize pulsing of the manometer levels. Normally, the calibrated manometer scale could be read to ± 0.02 cm. but under test conditions, and especially when the pulsing effects became noticeable, accuracy was reduced to ± 0.05 cm. Apiezon B oil was employed in the manometer on account of its low vapour pressure and density. The formation and detachment of the bubble was effected by means of the "Tombac" bellows system (*F*); a fine screw-thread on the spindle compressing the bellows ensured a slow and controlled rate of bubble formation.

The accurate positioning of the orifice in the liquid sodium was facilitated by a simple electric circuit (*H*). This circuit was "made" when the orifice tip first touched the sodium surface, on lowering the coaxial tubes (*C*) and (*D*). The lighting of the indicator lamp permitted the levelling arms, (*G*₁), attached to the tube (*D*), and (*G*), adjustable on a separate shaft, to be set at a zero position corresponding to the tip of the orifice resting on the liquid surface. The orifice tip could then be located at any depth in the liquid bath with an accuracy of ± 0.0005 cm. by means of a micrometer screw-gauge applied over the levelling arms. The bath temperature was recorded by a thermocouple carried in the sheath (*J*), placed within 2 cm. of the orifice tube. The sodium charge was introduced through a $\frac{1}{2}$ -in.-dia. stainless-steel tube (not shown in Fig. 3), which passed through the cover-plate of (*A*) and ended just above the top of the crucible (*B*); the sodium-handling techniques are described below.

Cleanliness of the apparatus was imperative, and all stainless steel parts coming in direct contact with sodium were electropolished before use; this applied to the internal surface of the sodium inlet tube. A high-vacuum system, capable of producing 5×10^{-6} mm. Hg, was attached, and thorough outgassing of all components was carried out before the sodium was introduced. High-purity argon, prepared by treatment over hot calcium and liquid sodium-potassium alloy, was used as a blanket gas during the determinations.

2. SODIUM-HANDLING TECHNIQUES

The sodium was high-purity distilled material,⁷ which analysed approximately 99.995% sodium, the impurities being boron 40, potassium 20, and oxygen 5–10 p.p.m. Steps were taken to maintain this

purity during transfer of the metal from the purification still, and the following two methods were used at different stages in the study. Preliminary sodium samples were transferred by means of a double-glass-bulb apparatus so designed that the sodium for the test came into contact only with the glass containers before its introduction into the surface-tension apparatus. Subsequently, for reasons outlined below, an all-metal apparatus was substituted for the glass one; a diagrammatic sketch of this is shown in Fig. 4. The vessel was filled directly from the purification still through the upper sodium valve and discharged into the apparatus by means of the lower valve; the central probe measures the volume of liquid sodium drawn off at each stage.

3. PROCEDURE

Before the introduction of sodium, the assembled apparatus was outgassed at 550° C. for 2 hr. under a vacuum of better than 5×10^{-5} mm. Hg and cooled. Exhaustive flushing with purified argon was then carried out, and finally a slight positive pressure,

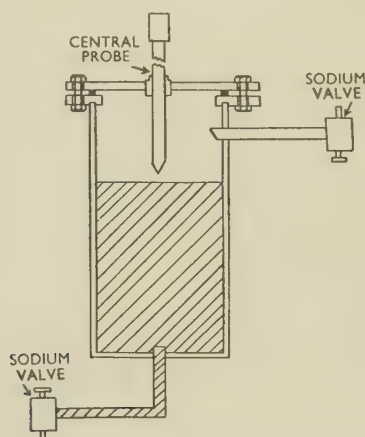


FIG. 4.—Steel-Bulb Sodium-Handling Apparatus.

relative to atmosphere, was set up in the entire system. A charge of some 250 c.c. of sodium was introduced in the manner described above. After the orifice had been located accurately at one of three depths, the maximum pressure required to form and detach several bubbles was determined by the slow compression of the bellows, the average of five or six readings being taken as the value at that level and temperature. Such values were recorded for three levels at each selected temperature, the three readings being made within a temperature range of $\pm 3^\circ$ C. of that recorded. The rate of bubble formation was not critical, provided that sufficient time was given for the meniscus to attain its equilibrium configuration. No variation in the maximum pressure recorded was found for rates of bubble formation less than six per minute.

Readings were taken over the temperature range from 110° to 450° C., on both heating and cooling cycles. Surging of the manometer levels, especially

at higher temperatures, imposed a limit of ± 0.05 cm. on the accuracy with which the pressure difference could be measured. This limit represents an overall accuracy of pressure measurements of $\pm 1.5\%$; the low density and relatively low surface tension of sodium mean that the pressure difference to be measured is small and the relative effect of this limit of accuracy is correspondingly serious. As it was considered that this pulsing resulted from convection currents in the argon atmosphere flowing between the hot area of vessel (A) (Fig. 3) and the water-cooled upper region, the steps outlined under Section III, 1 were taken to minimize this effect.

IV.—RESULTS

1. CALIBRATION TESTS WITH MERCURY

Initial calibration tests were carried out on mercury at 20° C., to estimate the accuracy of the physical measurements, e.g. manometer-fluid density, orifice

TABLE I.—The Surface Tension of Mercury at 20° C.

Density of manometer fluid	Density of mercury
= 0.862 g./c.c.	= 13.55 g./c.c.
First orifice radius	Second orifice radius
= 0.127 cm.	= 0.143 cm.

First Orifice		Second Orifice	
Orifice Depth, cm.	Surface Tension, dynes/cm.	Orifice Depth, cm.	Surface Tension, dynes/cm.
0.499	458.5	0.473	457.0
0.548	458.0	0.530	454.0
0.795	456.5	0.549	456.0
1.043	447.0	0.781	451.5
1.080	453.0	1.166	451.0
		1.168	448.5
		1.171	455.5
Average :	454.7	Average :	454.7

TABLE II.—Comparison of Surface-Tension Values for Mercury.

Author	Ref. No.	Method	Atmosphere	Surface Tension at 20° C., dynes/cm.
Present work	Max.-bubble-pressure	A	454.7
Bircumshaw . . .	9	" "	H ₂	469
Harkins and Grafton . . .	8	" "	Air	486
Hogness . . .	10	" "	H ₂	456
Harkins and Ewing . . .	11	Drop-weight	Vacuum	466
Siedentopf . . .	12	Sessile-drop	H ₂	436
Smith . . .	13	Capillary-rise	H ₂	436

diameter, &c., and to verify the assumptions made in regard to the method of bubble formation and the method of correction applied. A number of accurate values of the surface tension for mercury at 20° C. are available.⁸⁻¹³ Triple-distilled mercury was used in conjunction with orifice radii of 0.127 and 0.143 cm., the latter being selected so that, according to Porter's analysis, bubble detachment would take place from the external diameter. Sugden's method of correc-

tion, outlined in Appendix II (p. 152) was applied, and the resulting surface-tension figures are given in Table I; Table II compares the average value of these tests with figures previously reported.

The average surface-tension value for mercury at 20° C. obtained in the present tests was 454.7 dynes/cm., with a maximum scatter round the average of $\pm 2\%$. This compares excellently with the figure of 456 dynes/cm. given by Hogness,¹⁰ and is within 2.5% of the values given by Bircumshaw⁹ and by Harkins and Ewing.¹¹ This degree of agreement is considered satisfactory for the purpose of calibration.

2. SURFACE-TENSION VALUES FOR SODIUM

Preliminary results obtained with sodium handled in the glass apparatus showed a considerable scatter well outside the range of experimental error, and the temperature coefficient of surface tension on the cooling cycle was decidedly greater than that obtained on heating. Both effects focused attention on the

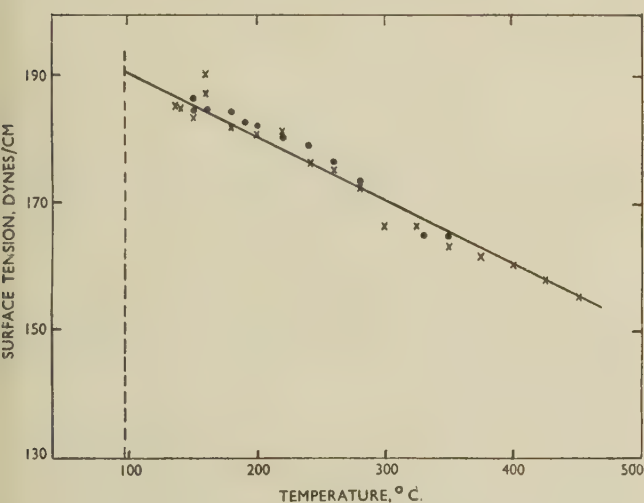


Fig. 5.—Surface-Tension/Temperature Relationship for Sodium (Heating Cycle).

x = Sample No. 1. • = Sample No. 2.

undesirability of using a glass bulb during initial handling, as the likelihood of contamination of the sodium was thereby increased. This led to the use of the metal container previously described.

The surface-tension values obtained from two separate samples of sodium handled in the metal container, are presented graphically in Figs. 5 and 6, the former representing values obtained on heating, the latter those obtained on cooling. The effective orifice radius for these measurements was 0.141 cm. The reproducibility of this group of results, as evidenced by two separate sodium samples (Fig. 5), was much better than that of the preliminary measurements. As judged from the scatter of the points about the best line relating surface tension to temperature, the overall accuracy appeared to be of the same order

as that of the pressure measurements, viz. $\pm 1.5\%$. These results lead to a value of the surface tension at the melting point (98° C.) of 190.8 dynes/cm., and of

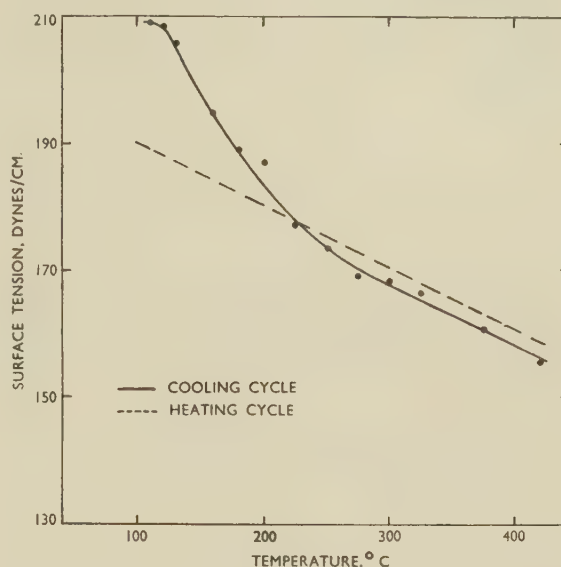


Fig. 6.—Surface-Tension/Temperature Relationship for Sodium (Cooling Cycle).

the temperature coefficient up to 450° C. of -0.1 dyne/cm./°C.

The values obtained on the cooling cycle (Fig. 6) show an anomalous maximum value of the order of 208 dynes/cm. at 120°–140° C., this effect being quite reproducible. During a subsequent investigation of this phenomenon, the sodium sample was held at a constant temperature of 130°–140° C., and surface-tension readings were recorded over a period of 80 min. The resulting isothermal time/surface-tension relationship is shown in Fig. 7. After passing through a maximum of 209 dynes/cm., the apparent surface tension dropped rapidly to a final value of 187.4

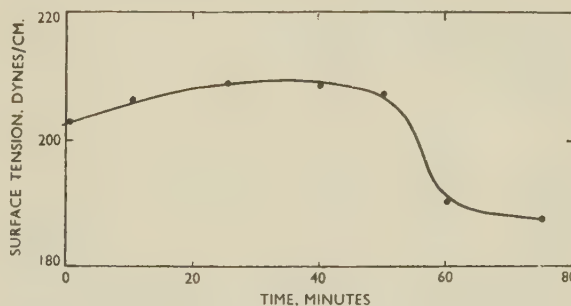


Fig. 7.—Isothermal Time/Surface-Tension Relationship.

dynes/cm.; the surface tension at 130° C. had a value of 187.9 dynes/cm. on the heating cycle.

3. DENSITY VALUES FOR SODIUM

The present experimental results were also used to establish a density/temperature relationship for

sodium, as the values thus deduced could be compared with the accurate relationship already established,³ thus providing an additional check on the accuracy of the measurements. By making pressure measurements at two or more depths, the surface-tension component of the maximum pressures may be eliminated, and density figures obtained from the relationship:

$$(\rho - \rho_0) = \frac{P_{\max,1} - P_{\max,2}}{(h_2 - h_1)g} \quad (5)$$

Subscripts 1 and 2 refer to different depths of immersion.

Owing to the small magnitude of the function ($P_{\max,1} - P_{\max,2}$) and the relative inaccuracy involved in such a difference, the individual density figures obtained showed a considerable scatter (Table III).

TABLE III.—Density of Sodium from Present Experiments and Previously Reported.³

Sample No. 1			Sample No. 2		
Temp., °C.	Density, g./c.c.		Temp., °C.	Density, g./c.c.	
	Exptl.	Reported		Exptl.	Reported
135	0.950	0.921	150	0.864	0.917
140	0.950	0.919	150	0.976	0.917
150	0.914	0.917	160	0.989	0.914
160	0.902	0.914	180	0.902	0.909
180	0.976	0.909	190	0.852	0.906
200	1.083	0.903	200	0.864	0.903
220	0.962	0.898	220	0.878	0.898
240	0.878	0.892	260	0.779	0.887
260	0.852	0.887	280	0.828	0.882
280	0.864	0.882	330	0.828	0.868
300	0.852	0.876	350	0.864	0.863
325	0.902	0.869	370	0.938	0.857
350	0.877	0.863			
375	0.816	0.856			
400	0.902	0.849			
425	0.841	0.842			
450	0.841	0.836			

By applying the method of least squares, the following relationship was derived between density and temperature:

$$\rho = 0.938 - 1.9 \times 10^{-4}T \quad (6)$$

The reported data conform to the equation:

$$\rho = 0.957 - 2.7 \times 10^{-4}T \quad (7)$$

Equations (6) and (7) are in good agreement, and even at 500° C. the discrepancy is only of the order of 2%. This may be regarded as an indirect check on the overall accuracy of the experimental measurements.

V.—DISCUSSION

1. EXPERIMENTAL RESULTS

The accuracy of the reported values is controlled by the error involved in the several physical constants

used in the final analysis. These constants and the estimated errors are:

Physical Constant	Estimated Error, %
Density of manometer fluid	±0.1
Density of sodium	±0.7
Orifice diameter	±0.7
Orifice depth setting	±0.1
Pressure measurement	±2.0

The major source of error is in the pressure readings and is accounted for by the pulsing of the manometer levels, especially at higher temperatures. Thus, it may be seen from Fig. 5 that the percentage error in the individual experimental values, represented by the deviation of the points from the linear relationship between surface tension and temperature, is of the same order of magnitude, i.e. ±1–1.5%, as the

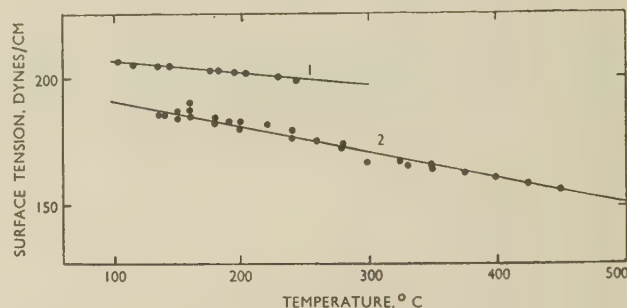


Fig. 8.—Comparison of Surface-Tension/Temperature Relationships Reported for Sodium. Curve 1: Poindexter and Kernaghan²; Curve 2: Present work.

error in the pressure readings. A similar order of accuracy is implicit in the density/temperature relationship derived, though in this case it must be recalled that the final relationship was arrived at by a statistical method.

A second possible source of error lies in the assumption that bubble formation and detachment occurred from the external orifice radius. According to Porter's analysis,⁴ if the contact angle fell below 90° the effective orifice radius would change from the external to the internal one. Had such a change taken place at any stage in the temperature range, an alteration of 30 dynes/cm. would have occurred in the surface-tension values over a short temperature range. That no such alteration was detected is taken to indicate that the effective orifice radius remained the same throughout the temperature range studied.

The present values are compared with those of Poindexter and Kernaghan² in Fig. 8. The present values are lower than those previously reported, e.g. 15 dynes/cm. lower at the melting temperature, while the temperature coefficient is twice that of the earlier workers. Such discrepancies are outside the range of experimental error of the two methods and must be attributed to a real difference in surface properties. It is suggested, for reasons outlined below, that the high values reported previously may be the result of an oxide film present on the surface of the sessile drop used by Poindexter and Kernaghan. Thus, in

the present study, the maximum value of 208 dynes/cm. obtained from the isothermal time/surface-tension relationship (Fig. 7), was considered to correspond to the formation of a complete oxide film on the surface of the bubble; this compares with the corresponding value of 205.5 dynes/cm. at 120° C. reported by Poindexter and Kernaghan.²

The presence of such an oxide film might also account for the lower temperature coefficient of the surface tension found previously. Although the solubility of oxide in sodium increases with temperature,³ the increase between 100° and 250° C., the range covered by Poindexter and Kernaghan, is only 30 p.p.m., and it is thus possible that an oxide skin would persist over this temperature range. Were this so, the observed temperature coefficient would not be that of sodium metal, and the presence of a strongly ionic surface film might be expected to reduce the temperature coefficient as a result of the increased mechanical strength thereby conferred on the bubble surface. It may be significant that Poindexter and Kernaghan's surface-tension value at 243° C., the highest temperature reached, falls below the projected line through values at lower temperatures (Fig. 8). Such an effect is consistent with the solution of the oxide film at the higher temperatures. Finally, a temperature coefficient of -0.05 dyne/cm./°C. is decidedly low for a metallic liquid, whereas the present figure of -0.1 dyne/cm./°C. is in general accord with values for other liquid metals and is in agreement with Skapski's¹⁴ calculated value of -0.09 dyne/cm./°C.

A similar increase in the apparent surface tension of aluminium, as a result of an oxide film at the surface, is reported by Portevin and Bastien;¹⁵ in air the apparent surface tension was 840 dynes/cm., whereas the corresponding value in purified argon was 300–420 dynes/cm.

The foregoing discussion of the two sets of results is closely related to the anomalous rise in surface tension observed during the cooling cycles (Fig. 6). Two separate experimental facts help to elucidate this effect. In the first place, the isothermal time/surface-tension relationship (Fig. 7) indicates that under these conditions the surface tension falls from its maximum value to one identical with that obtained during the heating cycle at the appropriate temperature. Secondly, when the argon used to form the bubble was progressively contaminated with oxygen, a surface tension greater by 21 dynes/cm. than the original value resulted at an oxygen concentration of approximately 5% by volume; the presence of an oxide film can thus increase the apparent surface tension of the sodium.

The following explanation of the observed anomalous increase in surface tension is accordingly proposed. During the heating cycle, traces of oxide, introduced during preliminary handling, are taken into solution. On cooling, the surface-tension/temperature relationship is normal until such time as the equilibrium solubility of oxide in sodium is exceeded;

in the case of sample No. 1 (Fig. 6) this occurred at 240° C., where the equilibrium solubility is reported as 50 p.p.m.³ Below this temperature oxide precipitation takes place from the supersaturated solution, and, occurring preferentially at the metal/gas interface, it results in a continuous film on the bubble surface with a consequent increase in the apparent surface tension. Such a film must be of a continuous nature, as particulate oxide would not be expected to have the observed effects on the surface tension and its temperature coefficient. In addition, the fact that the apparent surface tension increases rapidly as the temperature falls (Fig. 6) suggests that the film thickness increases as the temperature is reduced. This increase in film thickness is possibly related to the supersaturation effect indicated by Fig. 7, where a period of 50 min. was required for all the oxide to separate. Once oxide precipitation has stopped, the surface tension would be expected to fall to a value similar to that obtained on the heating cycle at a corresponding temperature. Such an explanation is also consistent with the increase of surface tension observed when using oxygen-contaminated argon; in this case the oxide film is formed *in situ* from the oxygen in the gas phase, rather than by precipitation from the liquid phase.

2. THEORETICAL CONSIDERATIONS

It is of interest, finally, to compare the value experimentally determined in the present work with surface-tension values predicted from several semi-empirical relationships and with those calculated from purely theoretical considerations.

Of the several empirical relationships that may be employed, one of the most accurate appears to be that between atomic volume and surface tension¹⁶ shown in Fig. 9. The surface-tension value now obtained

TABLE IV.—Correlation of Surface Tension and Physical Constants of Metals.

Metal	At. Vol., c.c.	L_0/σ	$\sigma A^{2/3} 10^{-2}$, dynes/cm.	$\sigma K'^{1/4} 10^{14}$, cm.	$1/(\sigma(\rho/A')^{1/3}) 10^{-6}$, c.c. dynes ⁻¹	f values
K . . .	47.7	...	26	66	1.4	0.53
Na . .	24.8	5.2	25	46	4.7	0.18
Cu . .	7.7	3.3	42	8	6.6	0.04
Zn . .	9.7	3.3	48	14	6.2	0.40
Ag . .	11.5	5.6	47	9	4.2	0.17
Cd . .	14.1	3.6	34	13	5.2	0.14
Sn . .	17.0	9.2	35	10	4.0	0.12
Pb . .	20.1	6.5	33	10	4.0	0.18
Au . .	11.6	6.5	58	6	3.4	0.16
Hg . .	14.8	2.4	28	17	6.0	0.45
Sb . .	21.5	7.2	27	10	4.3	0.16
Bi . .	22.8	7.5	28	11	4.8	0.14

A = Atomic volume. A' = Atomic weight. K' = Compressibility.
 L_0 = Heat of sublimation.

is in general accord with the inverse relationship between these two properties, but the accuracy of the relationship does not permit the selection of one experimental value in preference to another. The same is true of the several other relationships listed in Table IV, and little is gained by considering them in detail.

Purely theoretical calculations of the surface ten-

sions of metals can be grouped into two classes, depending on the basis adopted. Of the two, electronic theories have had limited success in predicting surface-tension figures with any degree of accuracy. This is best seen from Table V, where several theoretical values for the surface tension of sodium are compared with the present experimental value at the melting temperature. Only the treatments by Frenkel¹⁷ and by Stratton²² give results comparable

than the experimental values, owing to inaccuracies in the Sommerfeld free-electron model when applied to more complex metals. A recent paper by Ewald and Juretschke²⁴ discusses such inaccuracies in the theoretical calculations in some detail.

The alternative physico-chemical theories relate the surface tension and the cohesive properties of liquid metals and, while this approach is less fundamental than the electronic one, it appears to give a more accurate prediction of surface-tension values. Skapski,²⁵ from a consideration of the atomic groupings at the surface and in the interior of a liquid, has shown that the relationship between surface tension and cohesive energy should be of the form:

$$\sigma_0 = fL_0 \quad (8)$$

where σ_0 = Total molar surface energy at 0° K.

$$= n \cdot N^{1/3} (M/\rho)^{2/3} \left[\sigma - T \cdot \frac{d\sigma}{dT} \right]$$

n = packing fraction for surface atoms.

N = Avogadro's number.

M = molecular weight.

ρ = density of the liquid.

σ = surface tension at T° K.

$\frac{d\sigma}{dT}$ = temperature coefficient of surface tension.

L_0 = heat of sublimation.

f = proportionality constant.

For close-packed, non-associated liquids, $f = 0.25$ from a consideration of the number of nearest-neighbour bonds at the surface and in the interior of the liquid. The average value of f for liquid metals appears from Table IV to be nearer 0.16, with certain exceptions. From this discrepancy in f values, Skapski deduced that the metallic nature of certain liquids contributes a negative term to the surface tension. On this basis he calculated a value of σ_0 for sodium of 4190 cal./molar surface area, which is equivalent to a surface tension of 175 dynes/cm.; this is in reasonable agreement with the experimental figure now obtained of 191 dynes/cm.

Skapski's treatment has been criticized on two points by Oriani²⁶: (i) the conclusion that the metallic character of some liquids contributes a negative term to the surface tension, and (ii) the fact that the method of analysis is not generally applicable to all liquid metals. From a more detailed consideration of the packing of atoms at the liquid-metal surface, Oriani demonstrates that in fact the pairwise bonding at the surface is greater than in the interior of the liquid (a conclusion quite the opposite of that reached by Skapski). It is shown that there is a proportional relationship (Fig. 10) between the difference in pairwise bonding at the surface and in the interior of the liquid, ϕ , and the heat of sublimation, L_0 . Now ϕ is related to the total molar surface energy, σ_0 , and thus to the surface tension, by the expression:

$$\phi = \frac{2}{Z_s} \left[\left\{ \frac{Z_i - Z_s}{Z_i} \right\} \cdot L_0 - \sigma_0 \right] \quad (9)$$

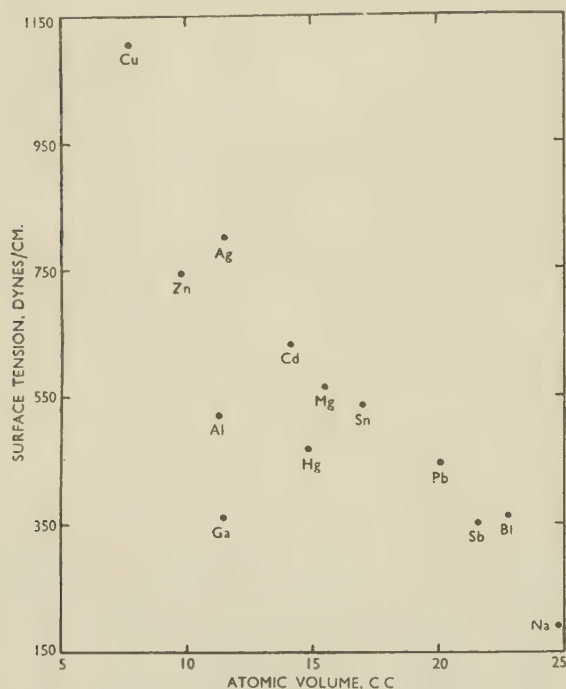


FIG. 9.—Surface-Tension/Atomic-Volume Relationship for Metals.

with the present work, and the former is theoretically unsound, since it is based on an ionic model for the structure of a metal. Stratton's calculations appear to be accurate for sodium, and it will be instructive to

TABLE V.—Comparison of Calculated and Experimental Values of Surface Tension of Sodium at the Melting Temperature.

Investigator	Ref. No.	Surface Tension, dynes/cm.	Method
Frenkel	17	190	Calculation
Gogate and Kothari	18	239	"
Samoylovich	19	363	"
Breger and Zhukovitsky	20	617	"
Huang and Wyllie	21	440	"
Stratton	22	190	"
Baldock	23	95	"
Present work	191	Experiment

compare his calculated values for lithium and potassium with the experimental values now being determined. The application of this wave-mechanical treatment to elements other than the alkali metals leads to surface-tension figures considerably lower

where Z_s = co-ordination number of atoms at the surface, and Z_i = co-ordination number of atoms in the interior. The value of ϕ deduced from the present experimental surface-tension data on sodium is in better agreement with the general (ϕ/L_0) relationship than is that from Poindexter and Kernaghan's data; the new value is designated Na' in Fig. 10.

It thus appears that the new surface-tension data are in agreement with the predictions of both the

The form of the bubble is related to the quantity B , where :

$$B = b^2/\beta^2 \quad . \quad . \quad . \quad (15)$$

Hence, from (14) and (15) :

$$\frac{r}{X} = \frac{r}{b} + \frac{r}{\beta\sqrt{2}} \cdot \frac{N}{b} \sqrt{\frac{B}{2}} \quad . \quad . \quad (16)$$

where

$$X = 2\beta^2/l \quad . \quad . \quad . \quad (17)$$

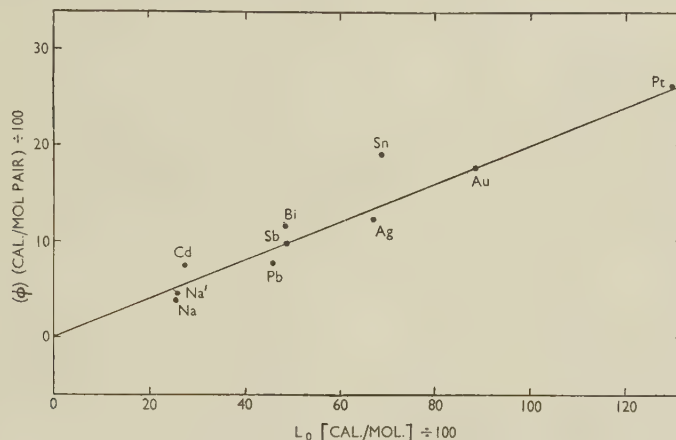


FIG. 10.— ϕ/L_0 Relationship for Metals.

physico-chemical treatments of the surface tension of liquid metals, but the final selection of the correct method of analysis must await a better understanding of the bonding characteristics of liquid metals.

APPENDIX I

*Sugden's Method of Correction*⁶

The general expression for the pressure difference ΔP across a meniscus, and its relation to the surface tension σ and curvature of that meniscus is :

$$\Delta P = \sigma(1/R_1 + 1/R_2) \quad . \quad . \quad (10)$$

where R_1 and R_2 are the respective radii of curvature. Considering the point O on the non-spherical bubble AOB (Fig. 11), the pressure at that point exceeds that at a point t cm. below the liquid surface by an amount :

$$\Delta P = \frac{2\sigma}{b} + Ng(\rho - \rho_0) \quad . \quad . \quad (11)$$

where b = radius of curvature at O , N = length OC , g = gravitational constant, ρ = liquid density, and ρ_0 = gas density. The pressure difference, ΔP , is equivalent to a column of liquid of height l where :

$$l = \Delta P/g(\rho - \rho_0) \quad . \quad . \quad (12)$$

From (11) and (12) :

$$l = 2\beta^2/b + N \quad . \quad . \quad (13)$$

where $\beta^2 = \sigma/g(\rho - \rho_0)$. Hence,

$$\frac{lr}{2\beta^2} = \frac{r}{b} + \frac{r}{\beta\sqrt{2}} \cdot \frac{N}{b} \cdot \frac{b}{\beta\sqrt{2}} \quad . \quad (14)$$

In equation (16), for any given value of $(r/\beta\sqrt{2})$, there are a number of values of (r/X) corresponding to a series of values of B , i.e. to a series of values of b . These values of (r/X) may be calculated from equation (16) in conjunction with tables compiled by

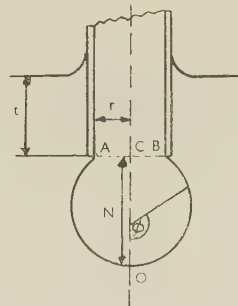


FIG. 11.—Bubble Dimensions Used in Sugden's Analysis.

Bashforth and Adams.²⁷ Thus values of (r/b) are first calculated from the expression :

$$r/b = r/\beta \cdot \sqrt{2} \cdot \frac{\beta\sqrt{2}}{b} = \frac{r}{\beta\sqrt{2}} \cdot \sqrt{\frac{2}{B}} \quad . \quad (18)$$

The corresponding values of the angle ϕ and the quantity (N/b) for this angle are obtained from the published tables²⁷ and inserted in equation (16) to calculate (r/X) . It is found that for a constant value of $(r/\beta\sqrt{2})$, (r/X) passes through a maximum at a certain value of ϕ . Hence, a table is drawn up relating maximum values of (r/X) to values of $(r/\beta\sqrt{2})$. The use of this table is illustrated in Appendix II.

APPENDIX II

Application of Sugden's Method of Correction to Mercury

Surface-tension component of the
maximum pressure = 6.29 mm. Hg.

Orifice radius = 1.27 mm.

First approximation to the quantity $(2 \cdot \beta^2)$

$$2\beta_1^2 = r \cdot l = 1.27 \times 6.29 \text{ mm.}^2$$

$$\therefore \sqrt{2}\beta = 2.82 \text{ mm.}$$

$$\text{Hence } (r/\beta_1\sqrt{2}) = 0.450$$

From Sugden's table,⁶ the corresponding values of $(X_1/r) = 0.875$.

$$\text{Hence } X_1 = 1.110 \text{ mm.}$$

Further approximations are carried out in an identical manner until a constant value of X is attained; in the present case, this was at $X = 1.09$ mm. The corrected surface tension is finally derived using this value of X in expression (4) (p. 145) of the main text.

ACKNOWLEDGEMENTS

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REFERENCES

1. G. L. J. Bailey and H. C. Watkins, *J. Inst. Metals*, 1951-52, **80**, 57.
2. F. E. Poindexter and E. Kernaghan, *Phys. Rev.*, 1929, [ii], **33**, 837.
3. R. N. Lyon, "Liquid-Metals Handbook", U.S. Department of the Navy and Atomic Energy Commission Publ. (NAVEXOS-P-733), 2nd edn., p. 114. 1952: Washington (U.S. Govt. Printing Office).
4. A. W. Porter, *Phil. Mag.*, 1930, [vii], **9**, 1065.
5. E. Schrödinger, *Ann. Physik*, 1915, [iv], **46**, 413.
6. S. Sugden, *J. Chem. Soc.*, 1922, **121**, 858.
7. G. W. Horseley, *Atomic Energy Research Estab. Rep.*, 1953, (**M/R.1152**).
8. W. D. Harkins and E. H. Grafton, *J. Amer. Chem. Soc.*, 1920, **42**, 2534.
9. L. D. Bircumshaw, *Phil. Mag.*, 1926, [vii], **2**, 341.
10. T. L. Hogness, *J. Amer. Chem. Soc.*, 1921, **43**, 1621.
11. W. D. Harkins and W. W. Ewing, *ibid.*, 1920, **42**, 2539.
12. H. Siedentopf, *Ann. Physik u. Chem.*, 1897, **61**, 235.
13. S. W. Smith, *J. Inst. Metals*, 1914, **12**, 168.
14. A. S. Skapski, *J. Chem. Physics*, 1948, **16**, 386.
15. A. M. Portevin and P. G. Bastien, *Compt. rend.*, 1936, **202**, 1072.
16. D. V. Atterton and T. P. Hoar, *Nature*, 1951, **167**, 602.
17. J. Frenkel, *Phil. Mag.*, 1917, [vi], **33**, 297.
18. D. V. Gogate and D. S. Kothari, *ibid.*, 1935, [vii], **20**, 1136.
19. A. Samoylovich, *Acta Physicochim. U.R.S.S.*, 1945, **20**, 97.
20. A. Kh. Breger and A. A. Zhukovitsky, *ibid.*, 1946, **21**, 13.
21. K. Huang and G. Wyllie, *Proc. Phys. Soc.*, 1949, [A], **62**, 180.
22. R. Stratton, *Phil. Mag.*, 1953, [vii], **44**, 1236.
23. G. R. Baldock, *Proc. Phys. Soc.*, 1953, [A], **66**, 2.
24. P. P. Ewald and H. Juretschke, "Structure and Properties of Solid Surfaces", edited by R. Gomer and C. S. Smith, p. 82. 1953: Chicago (University Press); Cambridge (University Press).
25. A. S. Skapski, *loc. cit.*, p. 389.
26. R. A. Oriani, *J. Chem. Physics*, 1950, **18**, 575.
27. F. Bashforth and J. C. Adams, "An Attempt to Test the Theories of Capillary Action". 1883: Cambridge (University Press).

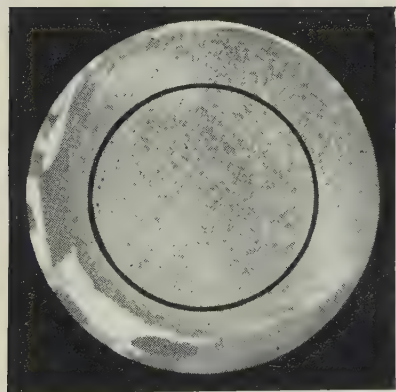


FIG. 1.—Macrostructure of H10 Rod Used in the Tests. $\times 3$.



FIG. 3.—Subsidiary Crack Illustrating Transcrystalline Fracture in H10 Rod. Untreated specimen tested in Birmingham tap-water. $\times 250$.

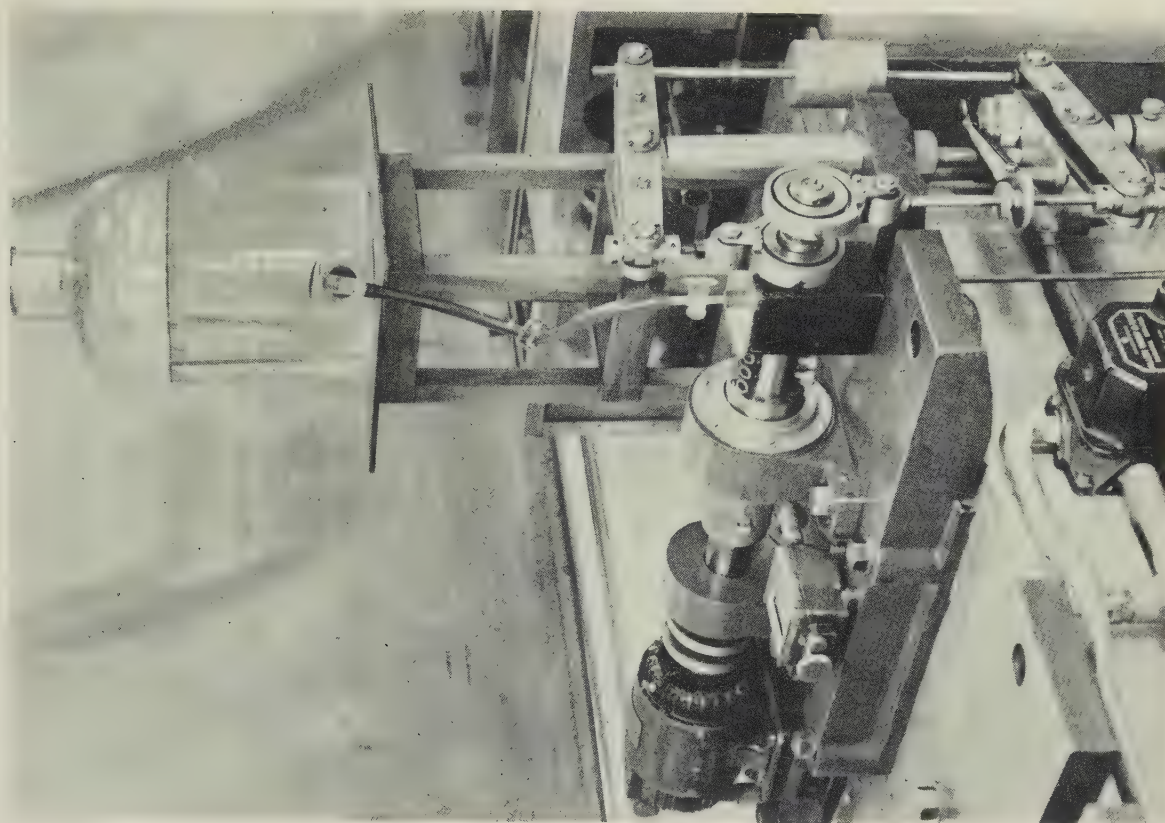


FIG. 2.—Wöhler Fatigue-Testing Machine, Showing the Two-Point Loading System and the Drip-Feed Arrangement for Corrosion-Fatigue Tests.

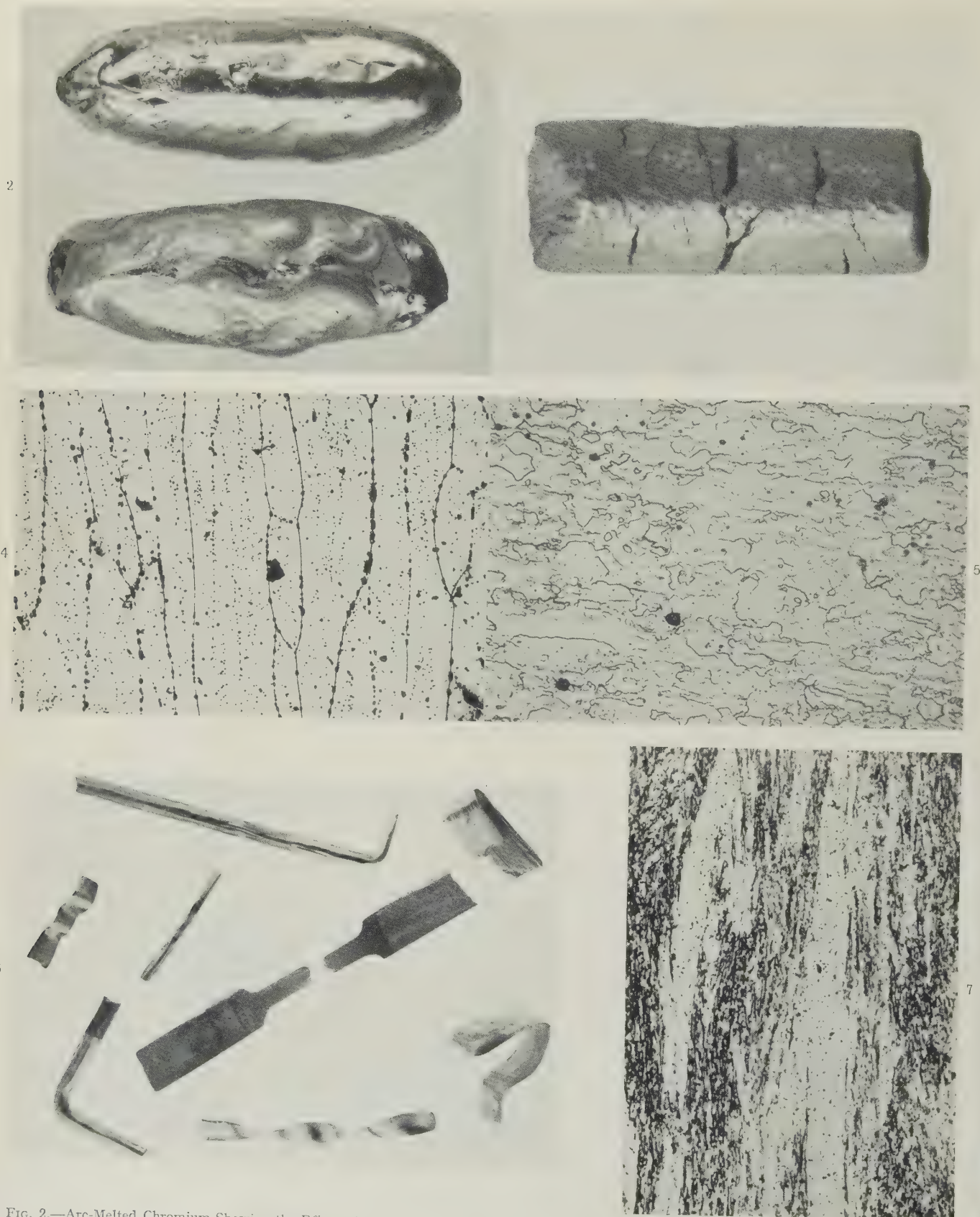


FIG. 2.—Arc-Melted Chromium Showing the Effect of Impurity Content on Surface Finish. The lower ingot contained 0.06 wt.-% oxygen and 0.005 wt.-% nitrogen, and the top one contained 0.02 wt.-% oxygen and 0.002 wt.-% nitrogen. $\times 1.5$.
 FIG. 3.—Cracking Caused by Forging a Cast Chromium Ingot Directly Without an Initial "Upsetting" Operation. $\times 2$.
 FIG. 4.—Microstructure of As-Cast Chromium, Showing the Columnar Grain Structure and Oxide Inclusions. Electrolytically etched. $\times 150$.
 FIG. 5.—Grain Elongation in a Longitudinal Microsection of Swaged Rod. Electrolytically etched. $\times 200$.
 FIG. 6.—Examples of Fabricated Chromium Deformed at Room Temperature.
 FIG. 7.—Chromium Rolled at 600° C., Showing Apparently Non-Uniform Deformation. Electrolytically etched. $\times 250$.

X-RAY BACK-REFLECTION PHOTOGRAPHS (*a*) AND PHOTOMICROGRAPHS (*b*) OF CHROMIUM SHEATH-ROLLED AT 560° C AND THEN ANNEALED.

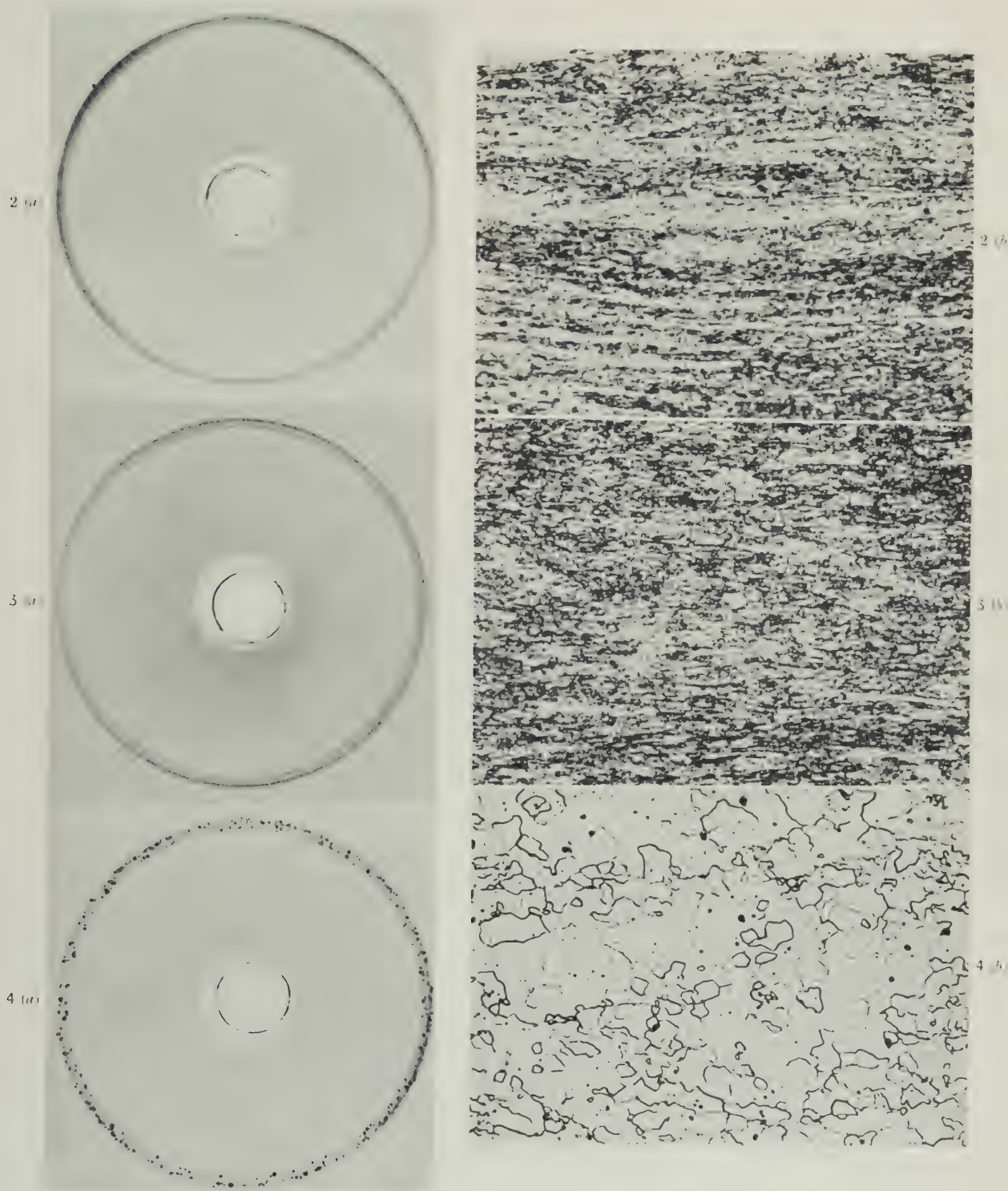


FIG. 2.—As-rolled at 560° C. (*a*) Diffuse rings. (*b*) Elongated grain structure. $\times 250$. Etched electrolytically in 10% oxalic acid.

FIG. 3.—Beginning of Recrystallization. (*a*) Annealed at 750° C. Sharp rings and a few sharp spots. (*b*) Annealed at 800° C. A few recrystallized grains in a cold-worked matrix. $\times 250$. Etched electrolytically in 10% alkaline potassium ferricyanide.

FIG. 4.—(*a*) Annealed at 850° C. Faint rings and many sharp spots. (*b*) Annealed at 850° C. Recrystallized grain structure. $\times 250$. Etched electrolytically in 10% oxalic acid.

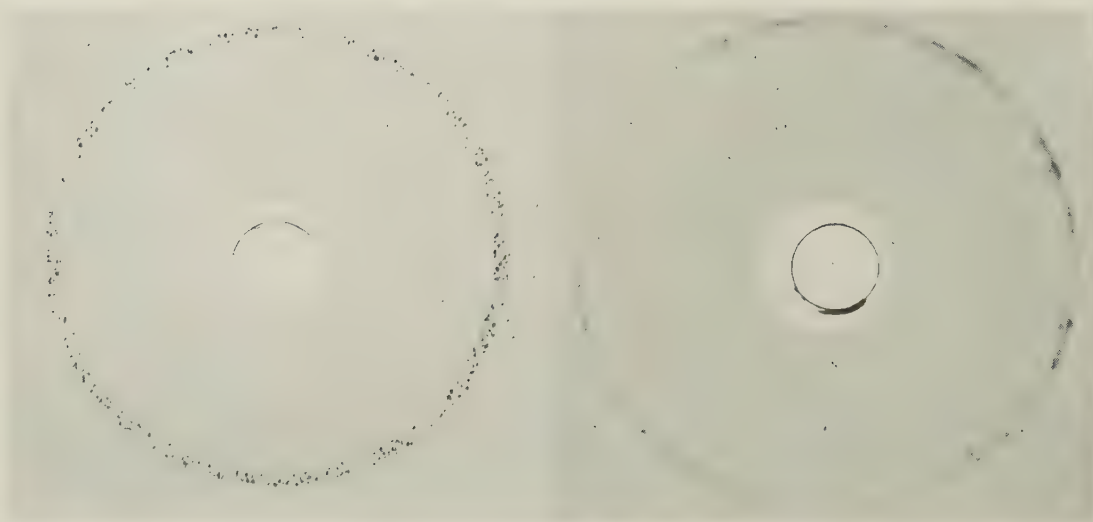


FIG. 5.—Chromium Rolled at 560°C . and Annealed at 900°C . Back-reflection photograph consists entirely of sharp spots, indicating complete recrystallization.

FIG. 6.—Recrystallized Chromium After Slight Deformation at 100°C . Back-reflection photograph shows some blurring of the spots from the recrystallized grains.

THE EFFECT OF INTERNAL OXIDATION ON THE FATIGUE PROPERTIES OF COPPER ALLOYS*

1580

By J. W. MARTIN,† M.A., Ph.D., JUNIOR MEMBER, and
G. C. SMITH,† M.A., MEMBER

SYNOPSIS

Polycrystalline and single-crystal specimens of copper containing dispersed non-metallic phases have been prepared by an internal-oxidation technique, and their fatigue properties compared with those of unoxidized material, using a constant-strain Chevenard microtorsion machine.

A reduced fatigue life, with intergranular fracture, characterizes the polycrystalline internally oxidized specimens. Internally oxidized single crystals have longer fatigue lives than annealed single crystals, the life depending on the fineness of the dispersion: the finer the dispersion of oxide particles, the longer the fatigue life at any given strain. The particles have been extracted, and their size range estimated by electron-microscopic examination.

I.—INTRODUCTION

IN the present investigation of the effect of dispersed non-metallic phases on the fatigue properties of copper alloys, the technique of internal oxidation has been used to produce suitable dispersions.

In this technique an alloy consisting of a dilute solid solution of a base metal in a more noble metal is heated under oxidizing conditions, when oxygen diffuses into the alloy, and a dispersion is produced of the oxide of the base metal in a matrix of the noble metal. The oxide may be in the form of particles or continuous films, depending upon the composition of the alloy and the oxidizing treatment.

A number of previous researches have dealt with the mechanical properties of internally oxidized materials.

Meijering and Druyvesteyn,¹ in work carried out in 1942, first showed that internally oxidized alloys in which a fine dispersion of oxide particles was formed underwent appreciable hardening and other changes in physical properties. Chaston² also discovered hardening in some internally oxidized silver alloys. On the other hand, Rhines³ reported that scratch-hardness tests gave no indication of an increase in hardness, although large increases were detected by micro-hardness indentation tests.

Recently, Smith and Dewhirst⁴ have investigated the internal oxidation of some dilute copper alloys. With very small particles, they found that the metal was hardened appreciably, an effect which was detected both by scratch and indentation measurements. Gottardi⁵ has studied a number of dilute silver alloys, and recorded increases in hardness on internal oxidation.

Smith and Gregory⁶ have examined the tensile properties at room and elevated temperatures of dilute silver alloys in the form of internally oxidized wires.

Whereas the hardness obtained by precipitation-hardening (in age-hardening alloys) is more or less destroyed by annealing at temperatures higher than the most favourable ageing temperature, the precipitates formed on internal oxidation proved to be more stable, so that the high-temperature properties of such alloys were of interest.

High creep-resistance has been reported by de Jong⁷ in internally oxidized copper-beryllium alloys. He particularly stressed the effect of grain-boundary segregation and lattice deformations of high stability.

No data have, however, been published dealing with the fatigue properties of internally oxidized materials and the study now described is concerned mainly with these properties.

No detailed attempt has been made to correlate quantitatively the fatigue results obtained with the type of dispersion produced, although the dispersed phases were examined in various ways.

II.—EXPERIMENTAL PROCEDURE

1. THE PRODUCTION OF A DISPERSED PHASE

Copper was chosen for the basis metal as being the most noble metal available in sufficient quantity at a reasonable cost, and the solute metals selected were silicon and aluminium. The alloys were supplied in the form of $\frac{3}{16}$ -in.-dia. wire by British Copper Refiners, Ltd., Prescot. Two methods of heat-treatment were adopted, depending on the time required, and all specimens were held in special holders made of compacted alumina.

(a) Long-Time Treatments

Certain internal-oxidation treatments lasted about three months, owing to the low temperatures selected and the size of the specimens. For these conditions,

* Manuscript received 29 January 1954; in revised form 1 September 1954.

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a method suggested by Rhines, Johnson, and Anderson⁸ was adopted, which consisted of embedding the specimens in a mixture of equal parts of cuprous oxide and copper metal powders. This is the equivalent of heating the alloy in an atmosphere having a partial pressure of oxygen equal to the decomposition pressure of cuprous oxide, and should maintain very nearly the saturation concentration of oxygen in the surface of the metal without allowing the formation of a primary cuprous oxide scale.

(b) Short-Time Treatments

The specimens were placed in a furnace tube, and held at the required temperature for $\frac{1}{2}$ hr. with an oxidizing atmosphere in the tube. This produced a copper oxide film on the surface of the specimens, and the main part of the heat-treatment was subsequently carried out in a neutral atmosphere, when the surface oxide film became the source of oxygen for the complete internal oxidation of the specimen. The neutral atmosphere was produced by passing oxygen-free nitrogen through the furnace.

In the case of copper-silicon specimens, the inner furnace tube was of silica, whereas the copper-aluminum specimens required a tube of thermal alumina.

2. THE FATIGUE-TEST METHOD

A Chevenard⁹ alternating-torsion fatigue machine was used. The specimens were relatively small, 1.5 mm. in dia. and of 8 mm. parallel test section, and were tested at constant strain. The machine records photographically couple-twist diagrams, and this was done at various stages during every fatigue test, and the diagrams subsequently analysed to yield information about the changes occurring during test.

A number of metallographic observations were also made. Torsion is a suitable form of testing for this procedure, as all changes occurring take place first at the surface, where they are readily detectable under the microscope.

3. PREPARATION OF SPECIMENS

(a) General Method

The shape and dimensions of the specimens used are shown in Fig. 1. Because of their small size, care was required to ensure that all the specimens were identical. They were "plunge" ground to a size slightly larger than that required, on an emery grinding wheel crushed to the profile of the specimen, and then polished with successively finer grades of emery paper down to 0000. Since this grinding and polishing might have distorted the surface and produced internal stresses, the finished specimens were always stress-relieved.

(b) Internally Oxidized Polycrystalline Specimens

Specimens 0.012 in. oversize on the final diameter were prepared from unoxidized material by the

"plunge" grinding technique. These partially finished specimens were then internally oxidized, but in order that they should have a uniform grain-size, a preliminary anneal *in vacuo* was given for $\frac{1}{2}$ hr. at the temperature at which the internal oxidation heat-treatment was to be carried out. This was necessary as otherwise the grain-size in the oxidized zone increases from the surface to the inner boundary, owing to restriction of grain growth by the oxide particles as they are formed. Thus the initial fine grain-size is observed at the edge, and the annealed grain-size appropriate to the temperature of oxidation at the centre.

The annealed specimens were inserted in the oxidizing furnace, and the heat-treatment was continued until the test section was fully oxidized. The

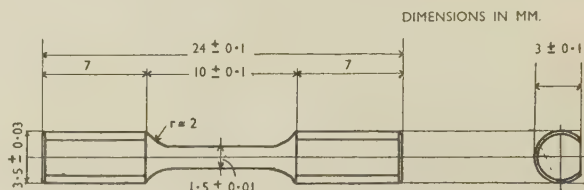


FIG. 1.—Form of Chevenard Fatigue-Test Specimen.

specimens were then removed from the furnace, put back on the grinding machine, and ground until they were just oversize. They were then polished to size and the surface finished with 0000 emery paper.

(c) Single-Crystal Fatigue Specimens

The crystals were grown by the Bridgman method of controlled solidification.

(i) Annealed

The specimens were "plunge" ground and the surface finished with 0000 emery paper in the ordinary way. The greatest care was exercised in removing the surface stresses introduced by the machining operations. In order to avoid recrystallization, the specimens were annealed *in vacuo*, being raised slowly from room temperature to 200° C., where they were held for 1 hr., and then allowed to cool in the furnace to room temperature. In this way it was possible to prepare test specimens as single crystals without recrystallization in the later stages.

(ii) Internally Oxidized

Since internally oxidized metal does not readily recrystallize, the crystals were oxidized before machining into specimens. It was found that when the rods which had been grown from the melt consisted of two or more crystals, then after internal oxidation the grain boundaries were clearly delineated as black lines, and the rod could be separated into its component crystals. The specimens were ground in the usual way, and stresses introduced during the machining operation were removed by giving a final anneal *in vacuo* for 1 hr. at 200° C.

4. FATIGUE-TEST PROCEDURE

The normal running speed of the Chevenard machine during a fatigue test is 1500 cycles/min. However, for recording the couple-twist diagram of the material at various stages of the fatigue test, a slower rate of straining of approximately 1 cycle/min. is used. The couple-twist loop obtained was analysed to obtain the value of surface shear strain and surface shear stress acting on the specimen. The area of the loop (ΔE), which is proportional to the energy dissipated per cycle by the specimen, and the overall slope of the loop ($\tan \beta$), i.e. the slope, with respect to the axis of strain, of the line joining the two ends of the loop, were also measured.

III.—FATIGUE TEST RESULTS

1. UNOXIDIZED MATERIALS

(a) *Pure Copper, Annealed at 700° C.*

The initial fatigue experiments were performed on oxygen-free high-conductivity copper having a grain-size of the order of 50μ , produced by annealing *in vacuo* at 700° C. The $\log S/\log N$ curve obtained, where S = strain and N = number of cycles to failure, is shown in Fig. 2. The changes in $\tan \beta$ and ΔE over the range of strain amplitude covered by this curve are shown in Fig. 4. Their general features will

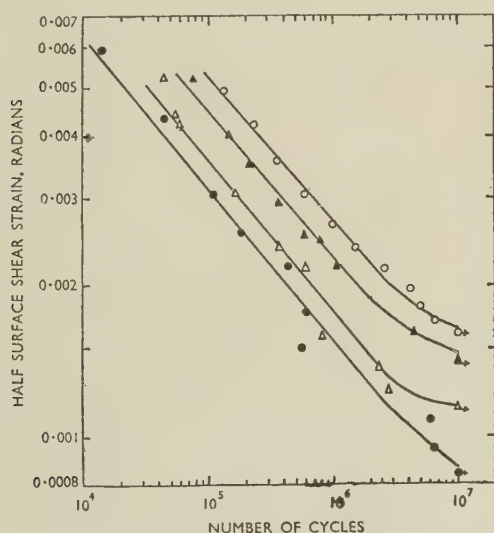


FIG. 2.— $\log S/\log N$ Curves for Annealed Copper and Copper Alloys.

KEY.

- Copper-0.3% silicon, single crystals.
- △ Copper-0.05% aluminium, vacuum-annealed at 900° C.
- ▲ Copper-0.05% aluminium, vacuum-annealed at 800° C.
- Pure copper, vacuum-annealed at 700° C.

be discussed later. The changes in the hysteresis loop were most marked at the beginning of each fatigue test, and couple-twist diagrams were therefore recorded after 0, 5, 10, 20, 50, and 100 kc. and thereafter at rather longer intervals.

In general, the largest changes in $\tan \beta$ and ΔE occurred between the first and second readings plotted in these curves. In view of this, the initial stage was investigated in more detail. The strain at which this was carried out was the maximum recorded on the

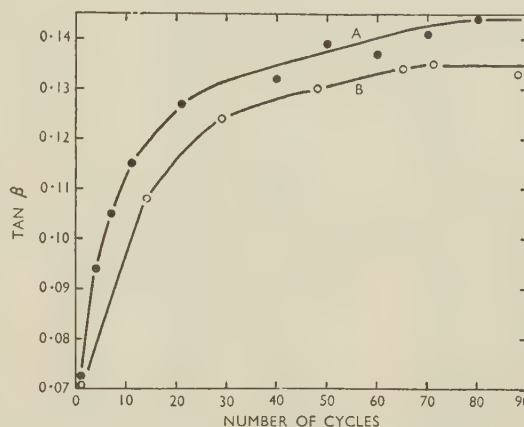


FIG. 3.—Initial Changes of $\tan \beta$ for Pure Copper Recorded at (A) Slow Speed, and (B) High Speed.

$\log S/\log N$ curve, namely 4.92×10^{-3} radians. Under these conditions the specimen life was approximately 130,000 cycles.

Curve A in Fig. 3, plotted over the first 150 cycles, was obtained by running at slow speed (i.e. driven by the slow-running motor normally used for the photographic recording of the couple-twist diagrams). The initial rapid rise in $\tan \beta$ took place over the first 70–80 cycles of the test, at this strain amplitude, and at this slow rate of test of approximately 1 cycle/min.

Curve B in Fig 3 was plotted to determine whether the results recorded in Curve A were a function of the low frequency at which the experiment was performed. The machine was run at the normal high speed between readings, the cycles being counted by winding a thread on to the main driving spindle during each run and noting the number of turns. Once again the initial rapid rise in $\tan \beta$ took place over the first 70–80 cycles of the test.

(b) *Copper-0.3% Silicon, Annealed at 900° C.*

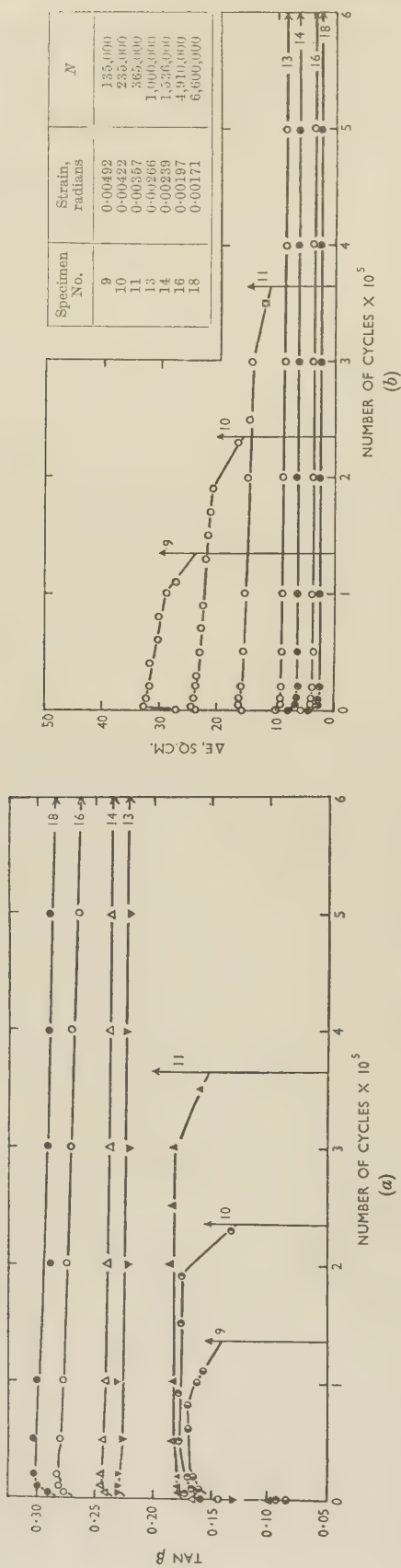
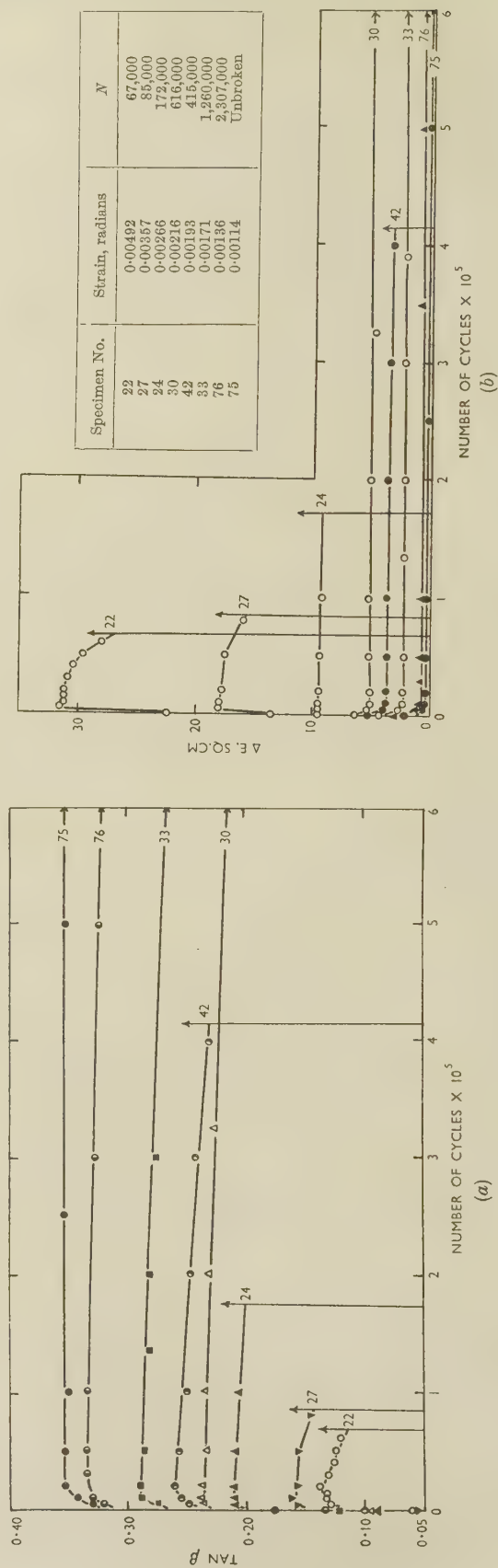
The fatigue properties were determined after annealing *in vacuo* for $\frac{1}{2}$ hr. at 900° C., giving a grain-size of the order of 250μ .

The $\log S/\log N$ curve is shown in Fig. 2. There was considerably more scatter in the results than with the fine-grained pure copper.

$\tan \beta$ and ΔE curves are given in Fig. 5 and have the same general characteristics as those in Fig. 4.

(c) *Copper-0.05% Aluminium, Annealed at 800° C.*

The fatigue properties were determined after annealing *in vacuo* for $\frac{1}{2}$ hr. at 800° C., giving a grain-size of the order of 150μ . Fig. 2 gives the $\log S/\log N$ curve. Less scatter was obtained than in the case of the coarser-grained 0.3% silicon specimens. The changes in $\tan \beta$ and ΔE are shown in Fig. 6.

Fig. 4.—Changes of (a) $\tan \beta$ and (b) ΔE up to 600 ke. for Pure Copper, Vacuum-Annealed at 700° C.Fig. 5.—Changes of (a) $\tan \beta$ and (b) ΔE up to 600 ke. for Copper-0.3% Silicon Alloy, Vacuum-Annealed at 900° C.

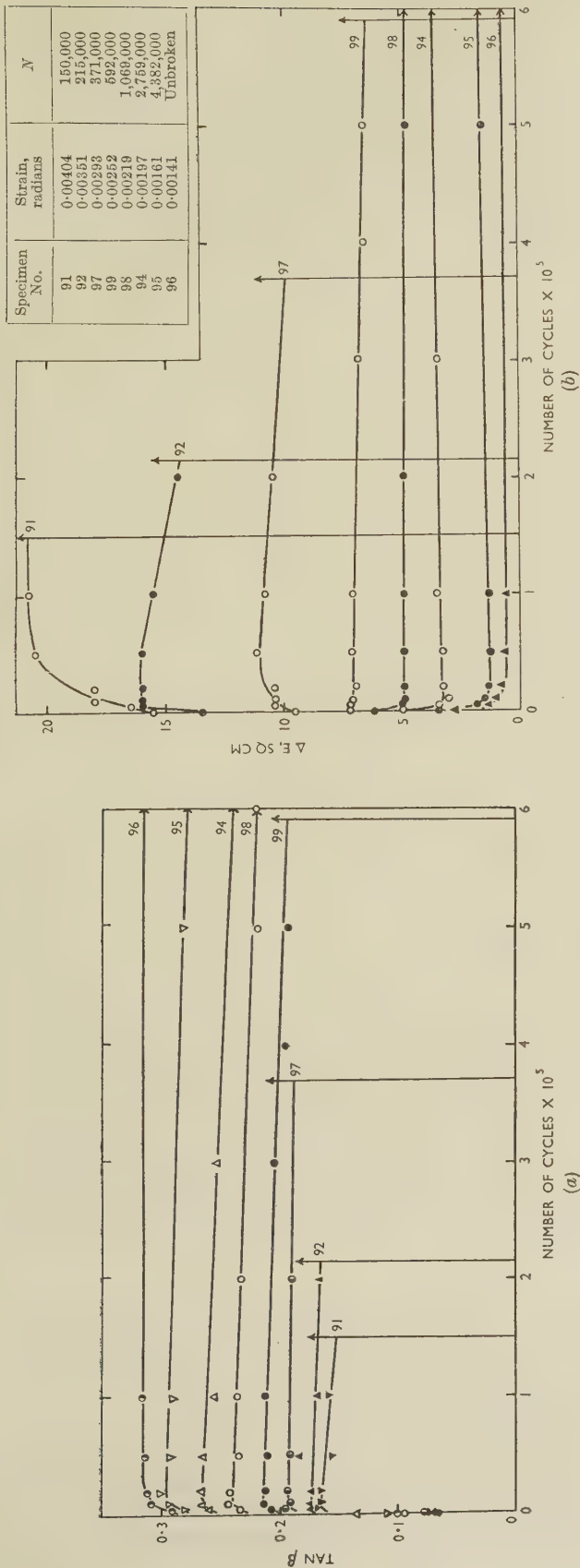


Fig. 6.—Changes of (a) Tan β and (b) ΔE up to 600 kc. for Copper-0.05% Aluminium Alloy, Vacuum-Annealed at 800° C.

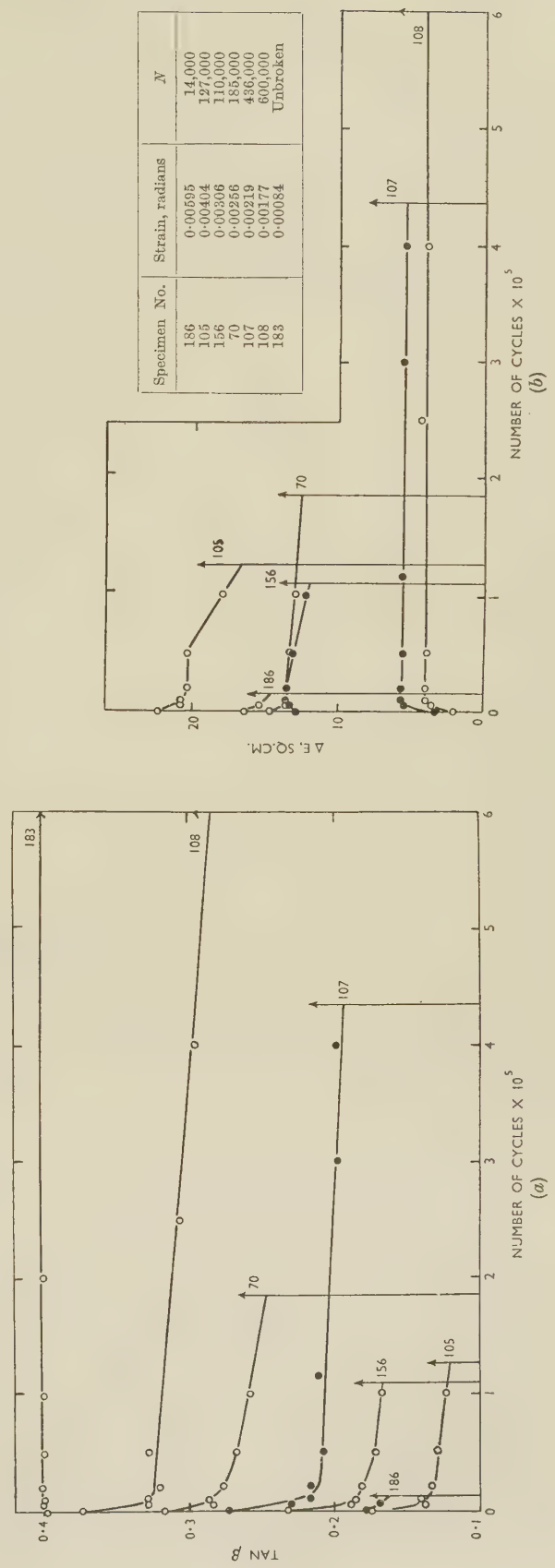


Fig. 7.—Changes of (a) Tan β and (b) ΔE up to 600 kc. for Copper-0.3% Silicon Alloy, Annealed Single Crystals.

(d) Copper-0.3% Silicon Single Crystals

The Bridgman method of controlled solidification used to prepare these specimens resulted in a [111] direction lying approximately along the axis of the specimen. This orientation was revealed by etching an electropolished section perpendicular to the axis, in concentrated ferric chloride, when (100) facets were produced, and the crystal could then be examined in a goniometer.

The $\log S/\log N$ curve is included in Fig. 2, and the changes in $\tan \beta$ and ΔE are shown in Fig. 7. The

(c) Copper-0.05% Aluminium, Oxidized at 800° C.

Fig. 8 includes the $\log S/\log N$ curve. Comparison with the curve obtained for the unoxidized material, annealed at 800° C., reveals that only a slight decrease in endurance resulted from the oxidizing treatment, as compared with the behaviour of the oxidized copper-0.3% silicon and copper-0.25% aluminium alloys. The fractures appeared to be only partially intergranular.

The changes in $\tan \beta$ and ΔE are illustrated in Fig. 12.

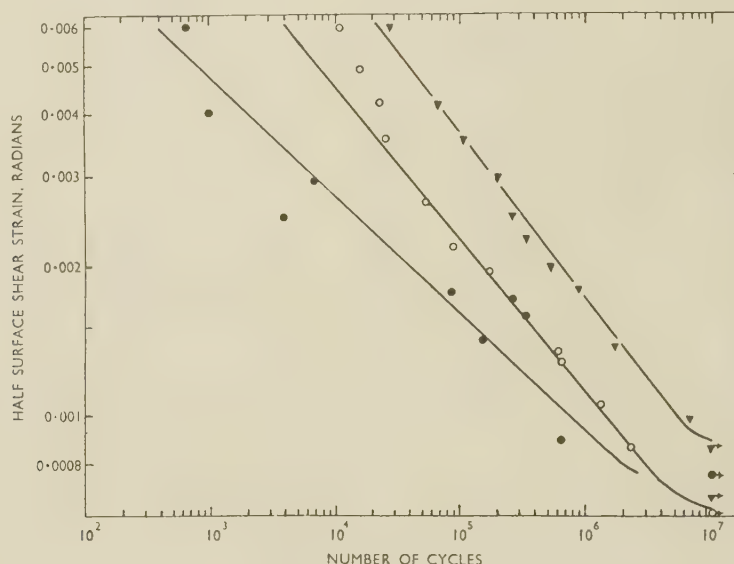


FIG. 8.—Log $S/\log N$ Curves for Internally Oxidized Polycrystalline Specimens.

KEY.

- ▼ Copper-0.05% aluminium, oxidized at 800° C.
- Copper-0.3% silicon, oxidized at 900° C.
- Copper-0.25% aluminium, oxidized at 800° C.

changes in the latter values differ somewhat from those obtained with the previous specimens, and will be discussed later.

2. INTERNALLY OXIDIZED POLYCRYSTALLINE SPECIMENS

(a) Copper-0.3% Silicon, Oxidized at 900° C.

The $\log S/\log N$ curve is reproduced in Fig. 8. Comparison with Fig. 2 shows that a reduced life resulted when this alloy was internally oxidized. The fractures were predominantly intergranular. The changes in $\tan \beta$ and ΔE are shown in Fig. 9.

(b) Copper-0.25% Aluminium, Oxidized at 800° C.

The $\log S/\log N$ curve is given in Fig. 8. The life was reduced to a very low value indeed at the higher strains, and all the fractures were characterized by their completely intergranular nature. The changes in $\tan \beta$ and ΔE are shown in Fig. 10.

3. INTERNALLY OXIDIZED SINGLE CRYSTALS

(a) Copper-0.3% Silicon, Oxidized at 950° C.

The $\log S/\log N$ curve appears in Fig. 11, and the changes in $\tan \beta$ and ΔE in Fig. 13.

Comparison of the $\log S/\log N$ curve with that for oxidized polycrystalline material indicates a considerable improvement in life. There is also a definite improvement in fatigue life over that of unoxidized single crystals.

(b) Copper-0.3% Silicon, Oxidized at 800° C.

To obtain a finer dispersion of oxide, some specimens were oxidized at 800° C., at which temperature approximately 13 weeks were required to oxidize completely the initial $\frac{3}{16}$ -in.-dia. rod.

Only one batch of specimens was prepared, and three points for this material appear in Fig. 11. If any significance can be attached to these isolated results, there was an improvement in life compared with the material containing the coarser dispersion of oxide.

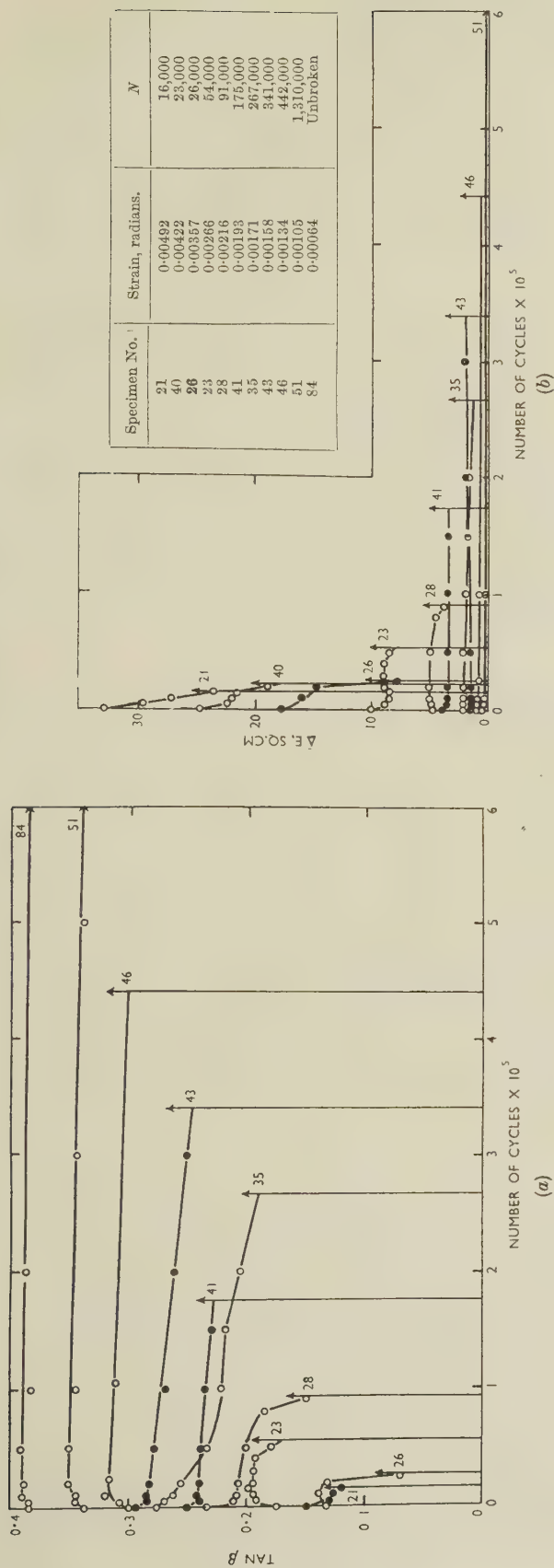


FIG. 9.—Changes of (a) Tan β and (b) ΔE up to 600 kc. for Copper-0.3% Silicon Polycrystals, Internally Oxidized at 900° C.

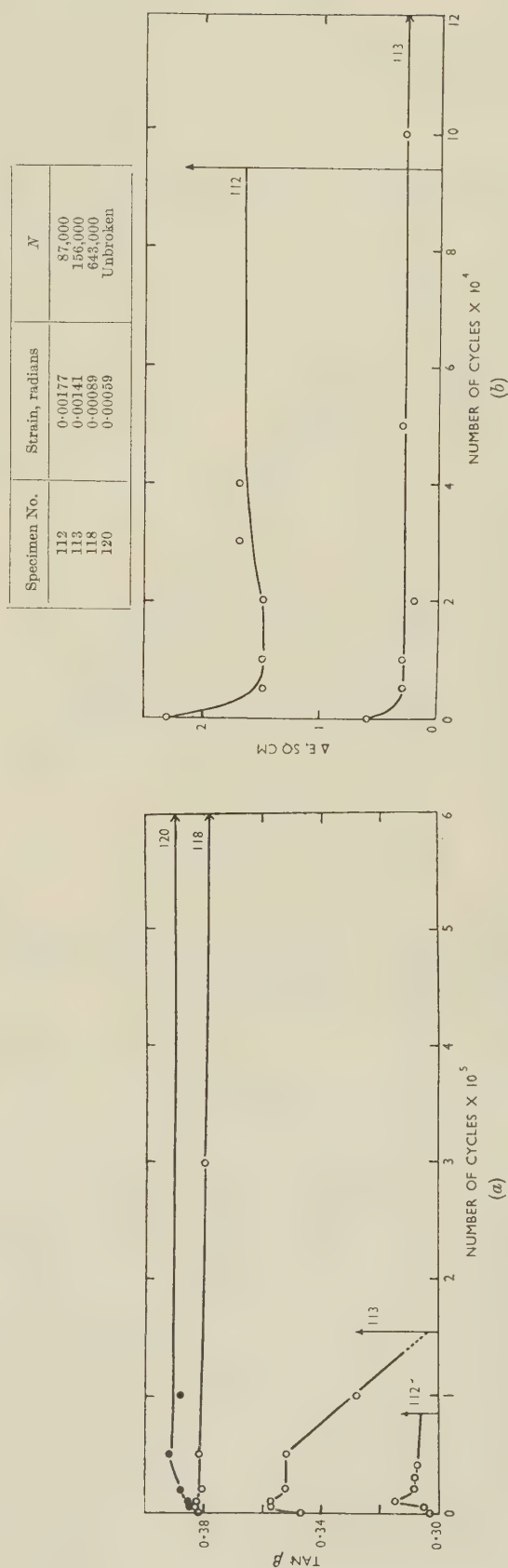


FIG. 10.—Changes of (a) Tan β and (b) ΔE up to 600 kc. for Copper-0.25% Aluminium Polycrystals, Internally Oxidized at 800° C.

The low degree of scatter generally noted in all the fatigue curves determined in the present work indicates that this is a real effect. The changes in $\tan \beta$ and ΔE are shown in Fig. 14.

(c) *Copper-0.25% Aluminium, Oxidized at 900° C.*

The $\log S/\log N$ curve is included in Fig. 11. Compared with the silica-bearing single crystals, this

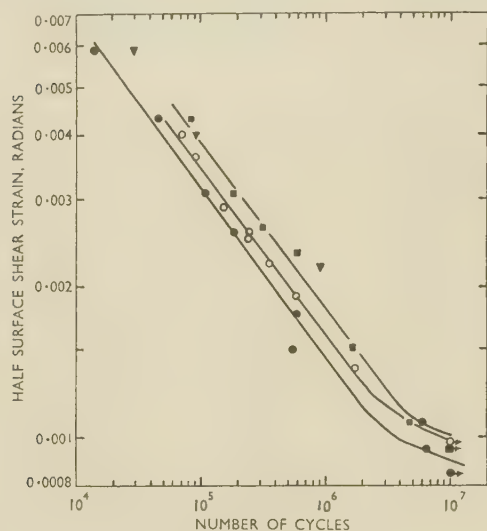


FIG. 11.— $\log S/\log N$ Curves for Internally Oxidized Single Crystals.

KEY.
 ○ Copper-0.3% silicon, annealed.
 △ " " " oxidized at 950° C.
 ■ Copper-0.25% aluminium, oxidized at 900° C.

shows a further improvement in fatigue life over that obtained with the unoxidized single crystals. $\tan \beta$ and ΔE curves are given in Fig. 15.

IV.—THE ANALYSIS OF THE DISPERSE PHASE

1. METHOD OF PARTICLE EXTRACTION

The metal containing the dispersion was dissolved in the minimum possible amount of 30% HNO_3 , and the solution and washings placed inside a synthetic semi-permeable membrane for dialysis.

For the first 10 hr., the dialysis was carried out against 10% HNO_3 , the solution being changed after every hour. The membrane with its contained suspension was agitated continuously in the liquid. After remaining overnight in 10% HNO_3 , it was dialysed for a further 24 hr. against distilled water, the water again being changed each hour during the first 10 hr. In this way all the copper salts were dialysed out of solution, and a suspension of oxide particles remained in the semi-permeable membrane.

A dialysis rather than a centrifuging technique was necessary, as in centrifuging there is a considerable

risk of losing the smallest particles unless the centrifuging times are very long.

2. THE NATURE OF THE DISPERSE PHASE

In the case of the internally oxidized copper-silicon alloys, a simple mineralogical test was devised to determine whether the disperse phase was in fact a form of quartz or whether it was an artificial spinel produced by the interaction of copper oxide and silica.

(a) Method

A suspension of the particles in water was prepared as described above. Several drops of the suspension on a microscope slide were dried by evaporation, and their refractive index estimated on a petrographic microscope by the Bekke "bright-line" method.

The particles were immersed in oils of various refractive indices and examined in each one. If the particles are in a medium of refractive index greater than their own, on defocusing upwards, a bright circle at the edge of each particle moves outwards from the particle; whereas if they are in a medium of lower refractive index, the bright line moves inwards to the centre of the particle.

(b) Results

With the oils available the refractive index of the particles was estimated to be just under 1.478 but over 1.45. Mineralogical text-books give the refractive indices of all known spinels as lying in the neighbourhood of 1.7. The form of quartz known as tridymite has the following refractive indices: $N_g = 1.473$; $N_m = 1.469$; $N_p = 1.469$.

It is therefore unlikely that the disperse phase is a spinel, as its refractive index is too low, and the results obtained indicate that it is tridymite. This is the form of quartz stable at the temperature of formation of the particles, namely above 800° C.

With regard to the dispersion produced on internally oxidizing dilute solid solutions of aluminium in copper, Meijering has demonstrated by a gravimetric technique that the oxide produced is consistent with the formula Al_2O_3 .

3. THE SHAPE OF THE DISPERSE PHASE

An electron microscope was employed to examine the extracted particles, the technique being as follows.

A number of electron-microscope copper grids were prepared with a thin collodion film covering them. A drop of the dialysed suspension was placed upon each of the grids by means of a capillary tube, and the grid left to dry in a dust-free container. The grids were then examined in a Siemens electron microscope.

(a) Silica Particles

An electron micrograph of extracted silica particles formed by internally oxidizing a copper-0.3% silicon alloy at 950° C. is reproduced as Fig. 16 (Plate XXV). The particles are spherical.

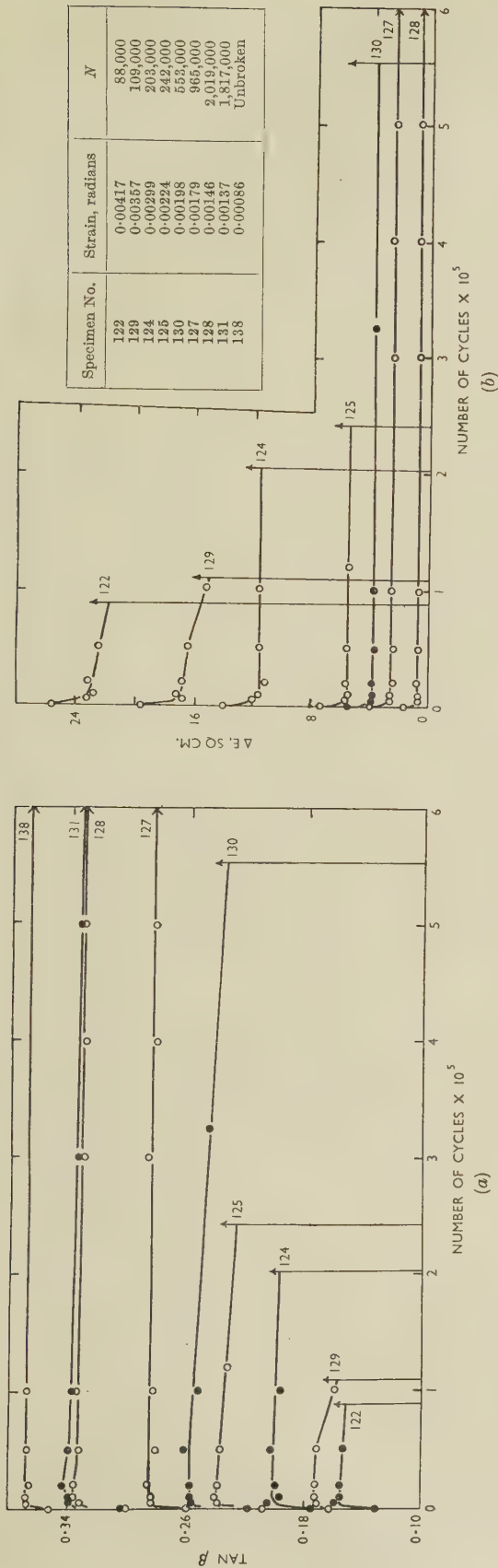


Fig. 12.—Changes of (a) $\tan \beta$ and (b) ΔE up to 600 kc. for Copper-0.05% Aluminium Polycrystals, Internally Oxidized at 800° C.

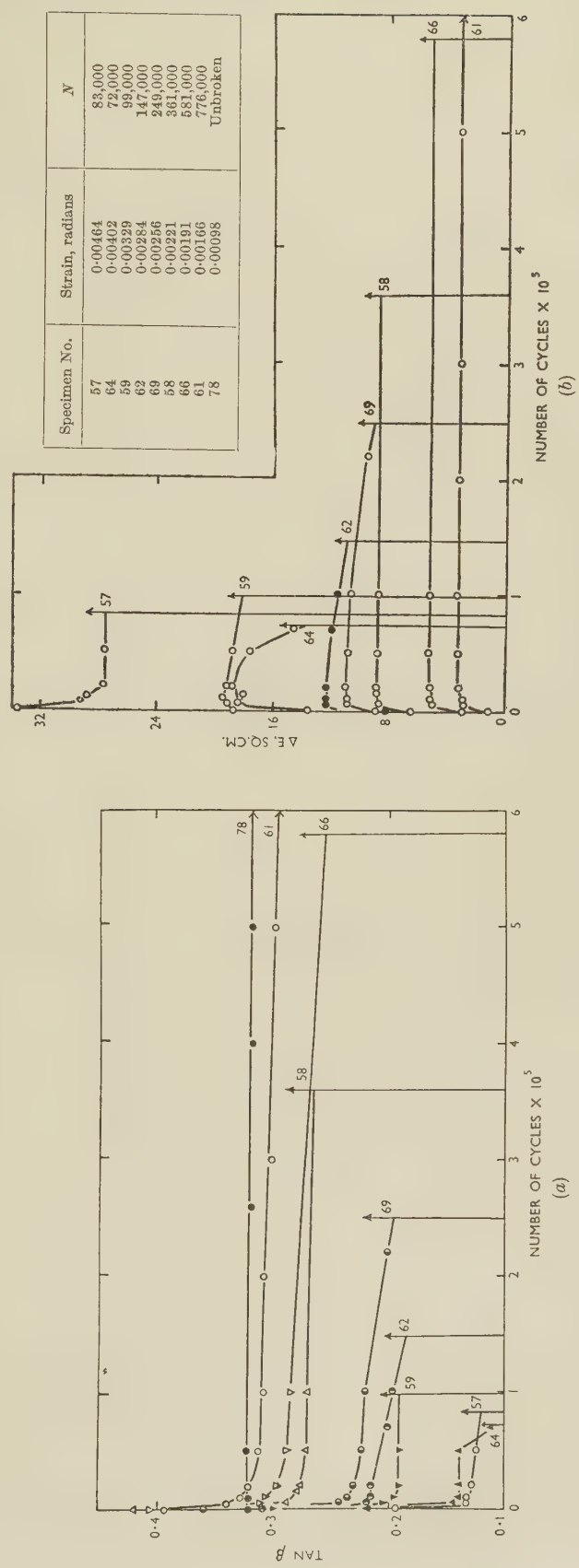


Fig. 13.—Changes of (a) $\tan \beta$ and (b) ΔE up to 600 kc. for Copper-0.3% Silicon Single Crystals, Internally Oxidized at 950° C.

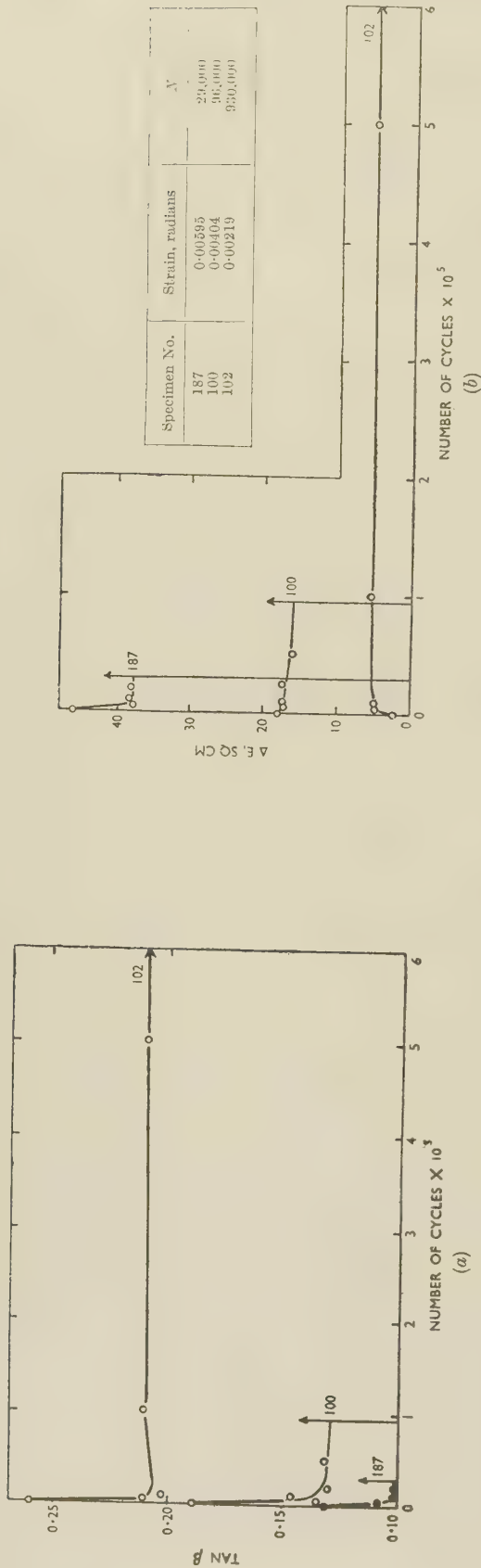


Fig. 14.—Changes of (a) Tan β and (b) ΔE up to 600 kc. for Copper-0.3% Silicon Single Crystals, Internally Oxidized at 800° C.

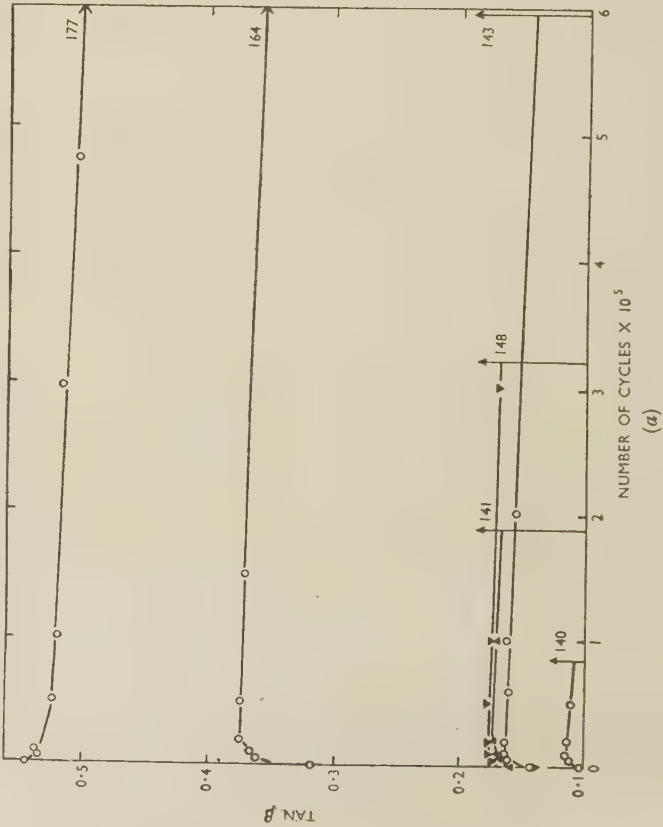
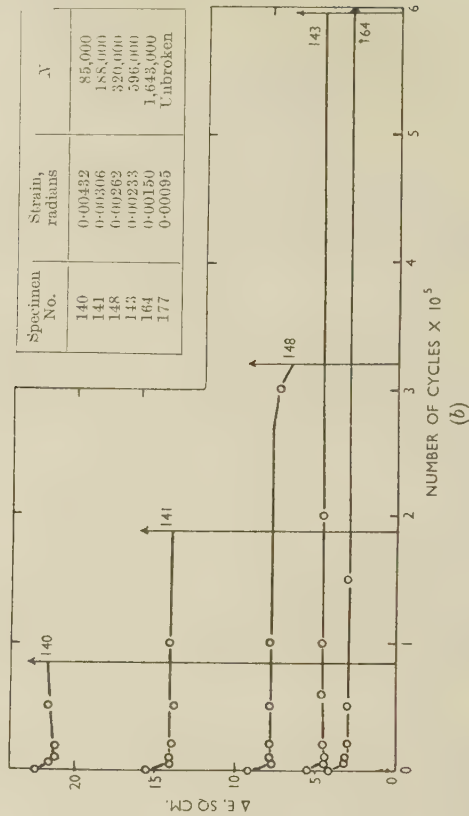


Fig. 15.—Changes of (a) Tan β and (b) ΔE up to 600 kc. for Copper-0.25% Aluminium Single Crystals, Internally Oxidized at 900° C.



(b) *Alumina Particles*

Fig. 17 (Plate XXV) is an electron micrograph of extracted alumina particles formed by internal oxidation of a copper-0.25% aluminium alloy at 900° C. The equiaxed nature of the particles is evident.

To test the effectiveness of this technique, a blank dialysis was performed. Some unoxidized material was dissolved and dialysed in the usual way. A drop of the dialysed liquid was placed on an electron-microscope grid, and subsequently examined. No trace of any mineral deposit could be detected, indicating that the dialysis routine adopted was sufficient to remove all soluble salts.

4. PARTICLE-SIZE ANALYSES

(a) *Method*

An analysis of the size of the oxide particles in the internally oxidized single-crystal specimens was made as follows.

As the particle distribution in the surface layers of the torsion specimens exercises the greatest influence on the mechanical properties, a layer one-quarter of the diameter deep was turned off a number of specimens of each type, and the turnings of each collected separately.

The particles were extracted by the technique described in Section IV, 1 and dispersed on electron-microscope grids in the usual way. A number of electron micrographs were taken of the particles under observation at a known magnification. Each plate was enlarged to obtain a print approximately 10 × 12 in. The diameters of the particles in the micrograph were determined with the aid of a photographic plate on which was printed a number of circular dots of increasing known diameter, and histograms were constructed to obtain a mean particle diameter.

(b) *Analysis of the Results*

Cumulative curves were constructed from each histogram. By replotting these cumulative curves on logarithmic-probability graph paper, the diameter of the particle having the average volume (d_v) may be calculated from the following formula, due to Dallavalle:¹⁰

$$\log_{10} d_v^3 = \log_{10} d_g^3 + 10.362 \log_{10}^2 \sigma_g$$

where d_g = geometric mean size (50% value
on log-probability plot).

$$\sigma_g = \text{standard deviation.}$$

$$= \frac{84.13\% \text{ size}}{50\% \text{ size}} = \frac{50\% \text{ size}}{15.87\% \text{ size}} \text{ (on log-probability plot).}$$

The results obtained in this way were :

For (i) Copper-0.3% silicon alloy,
oxidized at 950° C., $d_v = 5400 \text{ \AA}$.

For (ii) Copper-0.3% silicon alloy,
oxidized at 800° C., $d_v = 3200 \text{ \AA}$.

For (iii) Copper-0.25% aluminium alloy,
oxidized at 900° C., $d_v = 470 \text{ \AA}$.

V.—METALLOGRAPHY

Experiments were carried out on copper-0.3% silicon specimens in the oxidized and the annealed condition to determine and compare, by microscopical examination of the surface, the progress and extent of the deformation occurring during the fatigue test.

A specimen of the annealed material was electrolytically polished and etched in a methanol-nitric acid bath, the time of polishing being kept to a minimum to avoid reducing the section more than was necessary. This was followed by a light etch in acidified ferric chloride.

A fatigue test was carried out in the usual way, except that, in addition, the surface of the specimen was photographed before it was inserted initially in the machine; it was subsequently removed after various numbers of cycles in order to photograph the same area of the surface, being then replaced and the test continued.

The specimen was tested at a surface shear strain of 1.93×10^{-3} radians. Fig. 18 (a) and (b) (Plate XXV) show that fine slip lines are present after 5,000 cycles and that these have thickened considerably after 254,000 cycles (fracture).

Apart from the slight pitting evident in the photomicrographs, surprisingly little difficulty was encountered in electropolishing the oxidized specimens in the same bath as that used for the unoxidized alloys.

Fig. 19 (a) (Plate XXVI) is a photomicrograph of a specimen of alloy oxidized at 900° C. which had undergone 200,000 cycles at the same strain as that used for the unoxidized polycrystalline alloy. Fig. 19 (b) (Plate XXVI) shows the slip lines at a higher magnification; they appear to travel from particle to particle, and often to stop within a grain, and not to continue to a grain boundary.

Fig. 20 (Plate XXVI) illustrates the surface of the specimen just before the final fracture. The fatigue crack is intergranular.

A normal fatigue test was also carried out at a surface shear strain of 2.16×10^{-3} radians on a specimen of material oxidized at 950° C. A photomicrograph of the specimen in the region of the fracture after 575,000 cycles is reproduced as Fig. 21 (Plate XXVI).

The slip-line pattern appears more restricted in extent than is the case with annealed single crystals, and the path of the fracture appears to be parallel to the slip directions. A thorough examination of the specimen under the microscope showed that the fracture path was in fact always parallel to the traces of slip lines.

VI.—DISCUSSION OF RESULTS

1. UNOXIDIZED MATERIALS

The improved fatigue strength of the materials of finer grain-size was in accordance with expectation.

In the present tests more scatter was observed as the grain-size became coarser, since owing to the small size of specimen the grain diameter became comparable with the diameter of the specimen.

The surprisingly small degree of scatter obtained with the single crystals was no doubt due to the fact that their preferred orientation resulted in a [111] direction lying along the axis.

The general behaviour of the three types of polycrystalline specimen tested was found to be similar, and this aspect will be considered first.

(a) Polycrystalline Specimens

The changes in $\tan \beta$ and ΔE indicate that fatigue occurs in three main stages. Stage I covers the initial changes due to bulk plastic deformation and work-hardening. Stage II is an intermediate one, extending over the greater part of the life of the specimen, during which only relatively small alterations in bulk properties of the specimen can be observed. Stage III is normally short, and is concerned with the final stage of crack propagation and fracture.

During Stage I of the present tests, a rapid rise in the value of $\tan \beta$ was recorded, corresponding to the expected increase in the effective rigidity modulus due to work-hardening. During Stage II, which formed the major part of the tests, only a slight decrease in $\tan \beta$ was observed, and during Stage III (where detected) $\tan \beta$ decreased rapidly and continuously. Stage III is associated with crack propagation through the specimen, which effectively reduces the active cross-section, and both $\tan \beta$ and ΔE decreased in value during this stage up to fracture.

The investigations into the duration of Stage I are interesting in the light of the results of Sinclair and Dolan,¹¹ who concluded that disruption of atomic bonds, i.e. damage, was initiated in local regions "during a relatively early stage of cyclic stressing".

The metallographic changes observed can, to a certain extent, be correlated with the changes in $\tan \beta$. The work-hardening taking place during Stage I appears to be accompanied by the appearance on the surface of a fine array of slip lines. During Stage II, the new slip lines form in clusters constituting slip bands.

Thus, the $\tan \beta/N$ curve showing the rate of work-hardening may be regarded as consisting of two superimposed effects:

(i) A "transient" hardening curve, becoming approximately horizontal at the end of Stage I. This corresponds to the production of a fine array of slip lines throughout the structure.

(ii) A steady-rate curve obtained during Stage II, which becomes apparent only when the effects of curve (i) are reduced to a small value. This corresponds to the production of slip bands throughout the structure.

The magnitude of the change of ΔE during Stage I is the result of two opposing factors: (a) the decrease in width of the loop, and (b) the increase in $\tan \beta$, which will result in an increase in length of the loop,

since the test is conducted at constant strain. Factor (a) will tend to decrease ΔE and factor (b) to increase it, one or the other being predominant, depending on the fatigue life. For long lives (a) is predominant, and for short lives (b) predominates. The changes in ΔE are thus more difficult to assess, but in general the work-hardening of Stage I produces the expected decrease in ΔE . During Stage II, only small changes are observed, and in Stage III there is a steady decrease in ΔE up to fracture.

(b) Single-Crystal Specimens

As regards the copper-0.3% silicon alloy, the behaviour of $\tan \beta$ and ΔE in Stage I of the test was anomalous. Work-softening took place, resulting in a fall in $\tan \beta$ and a corresponding rise in ΔE . The reason is not readily apparent, but one possibility is that the silicon atoms in solid solution may give rise to this effect. For copper and silicon atoms, respectively, the Goldschmidt atomic diameters for 12-fold co-ordination are 2.551 Å. and 2.3458 Å., the silicon atoms being about 8% smaller than the copper atoms.

It is thus possible that solute-atom atmospheres are formed in the vicinity of dislocations, by analogy with the idea of Cottrell¹² regarding the distribution of carbon in steels. Cyclic stressing of the single crystals could then result in the dislocations being gradually torn from their anchoring solute atoms; a progressively lower stress would thus be needed for plastic deformation, causing ΔE to increase and $\tan \beta$ to decrease. This process would cease when strain-hardening began to predominate owing to the interaction of the freed dislocations. In support of this conception is the fact that an annealed single crystal of spectroscopically pure copper showed the same changes in $\tan \beta$ and ΔE as annealed polycrystalline specimens.

2. INTERNALLY OXIDIZED POLYCRYSTALLINE SPECIMENS

The intergranular weakness of the internally oxidized alloys is the most probable source of their lower fatigue life as compared with the unoxidized material. The grain interiors are at least as strong as those of the latter, but crack formation and propagation seem to be confined entirely to the weakened grain boundaries.

In specimens containing a dispersion of alumina, the changes in $\tan \beta$ and ΔE appear to be of a similar general form to those obtained with annealed specimens, and can be interpreted along the same lines.

The copper-0.3% silicon alloy, oxidized at 900° C., showed an anomalous behaviour in Stage I over certain ranges of strain amplitude. No clear explanation can be given for the observed changes in $\tan \beta$ and ΔE , as there are many factors operating which could have an effect. The tendency for $\tan \beta$ to decrease, as in the case of the oxidized single-crystal specimens discussed in the next section, will have superimposed upon it the tendency for an increase to occur by the

normal hardening effect observed in annealed polycrystals. In addition, the weakened grain boundaries doubtless represent another factor contributing to the observed changes.

3. INTERNALLY OXIDIZED SINGLE CRYSTALS

The fatigue tests carried out on single crystals, where grain boundaries and their associated detrimental effect are absent, reveal the true influence of the dispersed oxide phase.

The presence of the particles results in an improvement in fatigue properties, and the general indications are that as the disperse phase increases in fineness, that is, as the particle-size and mean spacing decrease, so the improvement in fatigue properties becomes more marked.

The observed changes in fatigue life with degree of dispersion are smaller than those observed in polycrystalline annealed materials with various grain-sizes. In the latter case the inhomogeneities, i.e. the boundaries, have a spacing of the order of 50–200 μ , whereas the oxide particles will have a mean spacing considerably less than this. Thus, the presence of the particles will exercise a more local effect on the movement of dislocations than do inhomogeneities such as grain boundaries.

During plastic flow of single crystals the movement of dislocations will be impeded by the presence of the dispersed particles. Following Fisher, Hart, and Pry,¹³ the dislocations may be regarded as forming closed loops about the particles, and the resultant hardening, and hence improved fatigue properties, can be attributed to the back stress from these entrapped dislocations inhibiting the movement of free dislocations. This back stress will depend upon the steady-state number of loops which each particle can support, and the manner in which they are distributed about it. It will clearly depend also upon the size and spacing of the oxide dispersion.

The changes in $\tan \beta$ and ΔE cannot be explained in any simple way. In Stage I of the test the behaviour was anomalous. Crystals containing the coarser dispersions, i.e. the silica-bearing materials, showed a fall in $\tan \beta$, in a similar way to the annealed single crystals. The alumina-bearing crystals, with a

finer oxide dispersion, exhibited a rise in $\tan \beta$ during Stage I more consistent with an initial work-hardening of the material.

The photomicrograph reproduced as Fig. 21 (Plate XXVI) shows that the path followed by the fatigue crack on the surface of these oxidized crystals is parallel to the slip directions. Although the amount of slip observed after fatiguing is less in internally oxidized crystals, nevertheless the slip bands will be associated in the surface with intense local deformation, and the nucleation of the final crack in these regions may reasonably be expected.

VII.—CONCLUSIONS

(1) The technique of internal oxidation has been employed for producing dispersions of non-metallic phases in copper alloys.

(2) The particles produced in this way are equiaxed in shape, and probably consist of a simple oxide of the base metal. During oxidation, a greater concentration of particles is formed in the grain boundaries than in the grain interiors, and this can lead to intergranular failure.

(3) The fatigue-resistance of polycrystalline specimens is decreased by internal oxidation, owing to the development of intergranular weakness.

(4) The fatigue-resistance of single crystals is increased by internal oxidation to an extent depending upon the fineness of the oxide dispersion.

(5) The mechanical and metallographic changes occurring during fatigue show that the process takes place in three main stages.

ACKNOWLEDGEMENTS

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REFERENCES

1. J. L. Meijering and M. J. Druyvesteyn, *Philips Research Rep.*, 1947, **2**, 81, 260.
2. J. C. Chaston, *J. Inst. Metals*, 1945, **71**, 23.
3. F. N. Rhines, *Atom Movements (Amer. Soc. Metals)*, 1951, 174.
4. G. C. Smith and D. W. Dewhirst, *Trans. Australian Inst. Metals*, 1950, **3**, 71; and *Australasian Eng.*, 1950, (Nov.), 61.
5. V. Gottardi, *Met. Ital.*, 1952, **44**, 424.
6. G. C. Smith and E. Gregory, to be published.
7. J. J. de Jong, *Ingenieur*, 1952, **64**, (28), O.92.
8. F. N. Rhines, W. A. Johnson, and W. A. Anderson, *Trans. Amer. Inst. Min. Met. Eng.*, 1942, **147**, 205.
9. P. Chevenard, *Rev. Mét.*, 1942, **39**, 65.
10. J. M. Dallavalle, "Micromeritics", 2nd edn. 1948: London and New York (Pitman).
11. G. M. Sinclair and T. J. Dolan, *Proc. 1st U.S. Nat. Congr. Appl. Mechanics*, 1951, 647.
12. A. H. Cottrell, *Phys. Soc.: Conf. on Strength of Solids*, 1948, 30.
13. J. C. Fisher, E. W. Hart, and R. H. Pry, *Acta Met.*, 1953, **1**, 336.

1581 AN APPARATUS FOR ELECTROPOLISHING SPECIMENS FOR METALLOGRAPHIC EXAMINATION *

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SYNOPSIS

An apparatus for electropolishing specimens of uranium or other metals is described, together with experiments with machines incorporating various methods of dispersing the anodic layer. The polished specimens are characterized by a complete freedom from flow lines produced by concentration of gas bubbles in the direction of flow of the electrolyte, as encountered with some units commercially available. The apparatus is cheap to build and is free from attack by even the most corrosive electrolyte likely to be used.

I.—INTRODUCTION

A PREREQUISITE for the accurate interpretation of the microstructure of metals is a suitably polished surface free from scratches, undesirable relief effects, and distorted material. Such surfaces, being difficult to prepare by mechanical means, are more conveniently produced by electrolytic polishing. This is particularly so in the case of uranium, since experience at the A.E.R.E.¹ has shown that the grain-size of this material is best examined under polarized light after electropolishing. Some information may be obtained by etching mechanically polished uranium specimens, but the detail is not as great as that given by examination under polarized light.

Many techniques for electropolishing uranium require the anodic layer to be continually removed from the surface of the specimen² if optimum results are to be obtained; this layer is usually removed by hand-wiping with a camel-hair brush. If more than a cursory examination is required, a considerable amount of distorted material has to be removed, necessitating electrolysis for 10 min. or longer, so that the brushing operation becomes very tedious and time-consuming. An investigation was therefore undertaken to develop an automatic machine which would produce electropolished surfaces of a quality at least equal to those obtained by techniques involving hand-brushing.

Modification of existing commercial machines was first considered, but a survey showed that these machines either did not provide for the removal of the anodic layer, or were constructed of materials which, while resistant to perchloric acid/alcohol and similar solutions, were not suitable for use with the highly corrosive electrolytes employed for electropolishing uranium, e.g. sulphuric acid/phosphoric acid/water solutions. The rather high prices of these pieces of apparatus militated against rebuilding them with resistant materials.

In some commercial units, a stream of electrolyte is directed across the face of the specimen and may result in gas bubbles collecting along the direction of flow, especially if the material contains inclusions of a second phase. This has the undesirable effect of producing channels in the polished surface which seriously interfere with examination at magnifications of up to $\times 250$. An attempt was therefore made to develop an apparatus based on A.E.R.E. experience of hand-operated electropolishing, in which the anodic layer and gas bubbles were continuously removed without the production of flow patterns on the surface of the specimen.

II.—DESIGN CONSIDERATIONS

It was desirable that the apparatus should be simple to construct, easy to operate, and have a long working life. Although primarily intended for electropolishing uranium, it would be advantageous if the machine were suitable for general use with a wide variety of metals.

Many electrolytes described in the literature^{3, 4, 5} for the electropolishing of various metals, including uranium, are solutions or mixtures of acids or alkalis, often in association with powerful solvents. The apparatus must therefore be constructed of easily fabricated materials having an extremely high resistance to these solutions, and not causing detonation of perchloric acid. With the exception of the platinum-group metals and tantalum, metals would probably corrode too rapidly, whilst glass and ceramics, besides being attacked by alkalis and fluorides, would be liable to fracture.

Of the available plastics, polyethylene ("Alkathene" or "Polythene") appeared most suitable for the construction of the apparatus. This material is a translucent, wax-like solid, inert towards alkalis and acids and to organic solvents at temperatures below 60° C. It is relatively easy to machine, becomes

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soft at temperatures over 100° C., and is weldable to itself, glass, or metal by heat applied by a cool soldering-iron or, preferably, by a stream of heated nitrogen. Polythene has a low coefficient of friction, but the very low thermal conductance and self-welding characteristics require that all continuously running bearings must be lubricated if seizing is to be prevented.

III.—DETAILS OF TESTS

Various uranium specimens were mounted in Bakelite and prepared for electropolishing by the standard method of grinding on paraffin-lubricated emery papers (grades 0, 00, 000) followed by mechanical polishing on two rotating felt pads fed respectively with coarse and "Microid 5/20" alumina. Electrical contact with the uranium was made by a brass pin passing through a hole in the back of the mount and held in place with Woods metal (fusible alloy). The following four electrolytes, which have been found the most useful for polishing uranium, were used for the tests.

(a) Sulphuric acid (sp. gr. 1.84)	200 ml.
Orthophosphoric acid (sp. gr. 1.56)	100 ml.
Water	200 ml.
(Mott and Haines ²)	
(b) Glacial acetic acid.	450 ml.
Perchloric acid (60%)	50 ml.
(c) Sulphuric acid (sp. gr. 1.84)	200 ml.
Orthophosphoric acid (sp. gr. 1.56)	100 ml.
Glycerol	120 ml.
Water	200 ml.
(d) Glacial acetic acid.	400 ml.
Chromium trioxide	85 g.
Water	100 ml.
(Saller and Rough ⁶)	

A series of machines was built, each incorporating a different method of removal or dispersal of the anodic layer, and the results obtained with them are summarized below.

1. ROTATING PROPELLER

The electrolyte was contained in a glass dish and continuously stirred by a glass two-bladed screw propeller; a uranium plate clipped to the side of the dish formed the cathode. The polish produced by this method was markedly inferior to that obtained by the hand-brushing method. The flatness of the surface deteriorated rapidly with time of polishing, and the contrast between grains under polarized light was poor. Increase in speed of stirring effected some improvement, but was limited by the tendency of the electrolyte to be thrown out of the dish by really vigorous stirring.

2. VIBRATING IMMERSED DISC

The general arrangement was similar to the above, but the propeller was replaced by a 2-in.-dia. resin-bonded paper diaphragm vibrated by an engraving tool at 50 c./s. with a maximum amplitude of $\frac{1}{8}$ in.

This device was found to be useless as a means of dispelling the anodic layer, as evolved gas tended to cling to the specimen, and the flatness of the surface deteriorated rapidly as electrolysis continued.

3. MOVEMENT OF SPECIMEN

The electrolyte was contained as before in a glass dish. When the specimen was moved by hand in arcs about 2 in. long, the surface was badly pitted, and soon became markedly inferior to that obtained by the hand-brushing method. Vibration of the specimen by the engraving tool in a direction perpendicular to the polished face caused the surface to become uneven and roughened, and gas bubbles adhering to the surface caused irregular polishing.

4. ROTATING WIPERS

The wipers were operated by a $\frac{1}{20}$ -H.P. geared variable-speed motor and formed of doubled, 0.003-in.-thick polythene film mounted with the cut edges uppermost in polythene arms which were revolved about a vertical axis. The brass contact pin of the specimen was screwed into the end of a vertical rod which could be rotated or held stationary. With a non-rotating specimen, the revolving wipers caused channelling of the surface in the direction of wiping, which appeared to be associated with evolved gases and was decreased by fitting multiple vanes to each wiper arm. The resulting surface was more satisfactory for examination at magnifications exceeding $\times 200$, although the contrast under polarized light was very good. Rotation of both specimen and wipers resulted in the production of a flat surface, together with excellent contrast when examined under polarized light.

An attempt was made to reduce the channelling effect by the use of two wiper arms alternately sweeping back and forth across the specimen in directions approximately at right angles. The surfaces produced showed slight channelling in two directions, but were brightly polished, and gave excellent contrast under polarized light. The apparatus was not further developed, however, owing to the difficulty of inserting and removing specimens quickly.

5. MACHINES UTILIZING A STREAM OF ELECTROLYTE

Removal of the anodic layer by the scrubbing action of a stream of electrolyte was first tested with a simple apparatus which gave very promising results, but the surfaces produced showed pronounced radial flow marks centred on the point of impingement of the jet of electrolyte. Variation of the rate of flow caused little difference in the severity of the flow marks. The contrast under polarized light was better than that obtained by the usual method of polishing involving removal of the anodic film by hand-brushing. When the electrolyte was circulated by an air-lift type of pump operated by compressed air, the surfaces obtained were fairly satisfactory but showed flow marks. Careful manipulation was required, the level of

electrolyte being particularly critical, and intermittent operation was caused by the evolved gases forming an insulating blanket over the specimen. The performance of this machine was considered sufficiently promising to justify the design of a second apparatus working on the same basic principles, but modified to overcome the defects outlined above.

6. MACHINE FINALLY ADOPTED

The initial apparatus was constructed largely from polythene reagent bottles. Preliminary tests using water with dye crystals as indicators had shown that a smooth but vigorous flow could be obtained by injecting electrolyte through a horizontal nozzle inserted

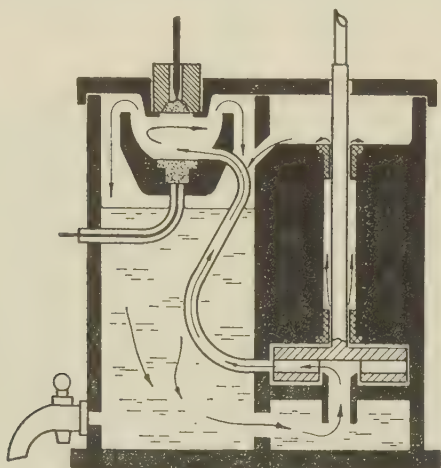


FIG. 1.—Schematic Diagram of Electropolishing Unit.

tangentially just above the bottom of a hemispherical bowl, and this feature was incorporated in an endeavour to eliminate flow marking of the specimen. The cathode was a $\frac{3}{4}$ -in.-dia. button of uranium set in the bottom of the polishing bowl. Electrolyte could be drawn from an external reservoir, or from the reservoir formed by the lower portion of the cell casing and was circulated by a centrifugal pump made of polythene and driven by a $\frac{1}{100}$ -H.P. variable-speed motor. To prevent seizure, the polythene bearings were lubricated by electrolyte, this being achieved by the use of a fully shrouded rotor in conjunction with a slightly restricted exit to produce a high-pressure region at the lower bearing, so causing electrolyte to flow upwards through the bearings, from which it was returned to the reservoir. The pump, when operating with water, delivered about 2.5 l./min. at a head of 6 in., and would maintain a static head of 4 ft. 3 in. A life test was discontinued after 200 hr., when the

pump did not seem to be impaired in any way. It is of interest to record that the prototype apparatus took about 20 man-hours to build and cost only £2 in materials.

A later and more compact form of this apparatus is illustrated in Fig. 1. The circulating pump was machined from $2\frac{1}{2}$ -in.-dia. bar and tack welded inside an oval outer casing formed by welding a length of partially flattened 5-in.-dia. polythene tube to a $\frac{1}{4}$ -in.-thick baseplate. The turned polishing bowl was internally $1\frac{1}{4}$ in. deep and $1\frac{1}{2}$ in. in dia., with a hemispherical bottom into which was fixed the uranium cathode. The bowl was held in position by three webs, and the electrical lead to the cathode was protected against corrosion by sealing inside polythene tubing. Mounted specimens could be slipped easily into the holder fixed to the lid and were retained $\frac{1}{32}$ in. below the top of the polishing bowl by the castellated rim of the holder. The outer casing formed a reservoir with a capacity of 500 ml.

This apparatus was extremely easy to use and electropolishing could be allowed to proceed without attention. The surfaces produced were superior to those obtained by hand-brushing, and there were no flow marks from concentration of gas bubbles in the direction of flow of the electrolyte. Even after prolonged electrolysis, the oxide particles in the uranium remained reasonably smooth and flat, and the contrast when examined under polarized light was excellent. The prolonged electrolysis makes possible the removal of a large amount of material, and in consequence surfaces prepared on this apparatus can be rendered almost entirely free from the effects of cold work arising from the mechanical polishing operations.

IV.—CONCLUSIONS

An apparatus has been developed for the electrolytic polishing of uranium without the need for constant and tedious brushing by hand of the surface of the specimen. The apparatus finally adopted is robust and cheap to build, yet produces a surface superior to that obtained by the more laborious method of hand-polishing. Unlike some commercial electropolishing units, there is no danger of the formation of flow marks on the surface of the specimen owing to the concentration of gas bubbles along the lines of flow of the electrolyte. Although the machine has been employed mostly for polishing uranium, equally successful results have been obtained with stainless steel, copper, and magnesium, and there appears to be no reason why its use should not be extended to other metals.

REFERENCES

1. B. W. Mott and H. R. Haines, *J. Inst. Metals*, 1951–52, 80, 621.
2. B. W. Mott and H. R. Haines, *Metallurgia*, 1951, 43, 255.
3. B. W. Mott and H. R. Haines, *J. Inst. Metals*, 1951–52, 80, 629.
4. E. C. W. Perryman, *Metal Ind.*, 1951, 79, 23.
5. D. S. Kemsley and W. J. McG. Tegart, *Council Sci. Indust. Research (Australia), Div. Tribophysics, Phys. Met. Rep. No. 7*, 1948.
6. H. A. Saller and F. A. Rough, *Trans. Amer. Inst. Min. Met. Eng.*, 1953, 197, 548.

SURFACE NUCLEATION IN THE RECRYSTALLIZATION OF ALUMINIUM SINGLE CRYSTALS *

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SYNOPSIS

Recrystallization nuclei in extended aluminium single crystals are found to lie preferentially in a surface layer about $2.5-5 \times 10^{-3}$ cm. deep. This surface-nucleation effect does not depend on crystal orientation (with one exception) or on specimen shape, and is also found in fine-grained polycrystalline aluminium. The effect can be eliminated by extending the crystal under an etching reagent, and is considered to result from the presence of an oxide layer on the crystal at the time of straining. An explanation in terms of piled-up dislocations is presented.

I.—INTRODUCTION

TIEDEMA¹ has reported that a single-crystal aluminium strip, oriented with a $\langle 112 \rangle$ direction parallel to the long axis and a $\{111\}$ plane parallel to the strip surface, will not recrystallize after 20% extension even when heated almost to the melting point, provided that the crystal is heavily etched after extension but before annealing. The same crystal would recrystallize if a region of severe local distortion was provided, as by a pin-prick or scratch, thus indicating that the failure to recrystallize was due to a lack of recrystallization nuclei.

In the course of recent experiments at the University of Birmingham, it was found that etching the surface of extended aluminium single crystals of various orientations had a similar effect in reducing the number of recrystallization nuclei.² The work described here was undertaken to provide further information about the role of the surface in the formation of recrystallization nuclei.

II.—EXPERIMENTAL PROCEDURE

1. MATERIAL

The material used for all the experiments was aluminium of nominal 99.6% purity (principal impurities being 0.19% iron and 0.13% silicon), in the form of cold-drawn (40% reduction in area) wire of 4.5 or 5 mm. dia., or as cold-rolled (40% reduction in thickness) strip 1 cm. \times 1 mm. in cross-section.

2. PREPARATION OF SINGLE CRYSTALS

Single crystals were prepared by the strain-anneal method. The cold-worked wire or strip was recrystallized for 15 min. at 650° C. to produce a fine,

uniform grain-size. Wire samples were extended 2.1–2.5% and strip samples 1.9%, after which the specimens were pulled at 2.5 cm./hr. through a tube furnace controlled at 650° C. This treatment produced single crystals of 25 cm. or more in length.

The crystal orientations of the wire samples were determined from back-reflection Laue photograms to an accuracy of $\pm 1^\circ$. The Laue reflections showed no evidence of a sub-structure. Orientations of the strip specimens were determined by measuring etch

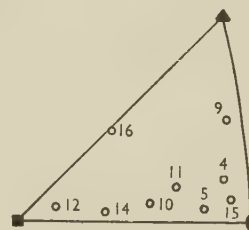


FIG. 1.—Crystal Orientations of Tensile Axes of Crystals Examined.

pit reflections with a two-circle optical goniometer to an accuracy of $\pm 2^\circ$. The orientations and identification numbers of the crystals examined are shown in Fig. 1.

3. RECRYSTALLIZATION

Each crystal was extended in a simple hand-operated tensile machine. In certain cases the extension was carried out with the crystal immersed in a bath of an etching reagent. After extension, the grip ends of the specimen were cut off, and the crystal cut into lengths of 3–4 cm., using a jeweller's saw. The samples so obtained were etched for varying periods of time in one of the following reagents: hot

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(70°–90° C.) 10% sodium or potassium hydroxide, 3% orthophosphoric acid, boiling *aqua regia*, or Flick's etch (10 parts HF, 15 parts HCl, 90 parts H₂O). The amount of material removed by etching was measured by micrometer.

After etching, the samples were annealed for 15 min. in an electric-resistance furnace controlled at $600^{\circ} \pm 5^{\circ}$ C. All the samples of each set (cut from the same single crystal) were annealed together, so that their heat-treatments were identical.

The recrystallized grain-size was revealed by etching with Barrett and Levenson's reagent (9 parts HCl, 3 parts HNO₃, 2 parts HF, 5 parts H₂O). In an attempt to derive quantitative information, grain counts were made on one or two specimens, but the grain-size was so large and irregular that the results were of doubtful significance. Consequently, no further counts were made, and the effects of etching were determined by direct visual comparison between the samples of each set. As can be seen from the accompanying photographs (Figs. 2–6, Plate XXVII), this simple procedure was quite adequate, because of the large changes in grain-size found.

III.—RESULTS

Fig. 2 (a)–(f) shows a typical set of results for a crystal (No. 5) extended 20%. Etching with 3% phosphoric acid, which has been reported to remove only the oxide layer,³ slightly increased the recrystallized grain-size (b), as did a light etch in hot 10% potassium hydroxide (c). A heavier hydroxide etch, however, (d)–(f) caused a very marked increase in the recrystallized grain-size—so much so that only three or four grains were found in the sample, apart from the small grains obviously nucleated at the cut ends as a result of the sawing operation.

The same result was obtained when the heavy etching was carried out in boiling *aqua regia* instead of in potassium hydroxide, as shown for crystal No. 4 in Fig. 3 (a)–(f). The shape of the sample had no significant effect, as similar results were obtained using strip samples (crystal No. 16, not illustrated).

Increasing the extension from 20 to 50% produced a finer recrystallized grain-size for all amounts of etching, but did not eliminate the surface-nucleation effect (crystal No. 10, not shown).

Etching sample (a) of Fig. 2 to half its original diameter revealed no change in the grain-size, indicating that the fine grain-size of the unetched samples extended to the interior of the specimen.

In a number of cases where only a few large grains were obtained on recrystallization, the orientations of these grains were determined, to ensure that they were, in fact, recrystallized grains. In all cases, the change in orientation showed conclusively that recrystallization had taken place.

To obtain information about the effect of very light etches, one set of samples (crystal No. 11) was etched in a slow-acting medium, after extension, and the

amounts of material removed were determined by weighing each sample to the nearest milligramme before and after etching. The results of this test, shown in Fig. 4 (Plate XXVII) indicate that the surface-nucleation effect is not eliminated until more than about 4×10^{-3} cm. of material has been removed.

To rule out the possibility that the above results might be due to surface contamination acquired in the wire-drawing or other manufacturing process, a sample wire was etched to half its original diameter before extension. The surface-nucleation effect was still present.

The surface-nucleation effect has also been found in this laboratory⁴ in an aluminium single crystal of 99.992% purity, indicating that the effect is not confined to lower-purity material.

Crystal No. 12, which had an orientation near $\langle 100 \rangle$ (see Fig. 1), showed a much finer recrystallized grain-size than any other crystal examined, and etching after extension had no effect on the recrystallized grain-size. This anomalous behaviour, which was not observed in any other crystal, is thought to be due to the unusual crystal orientation, which leads to complex deformation behaviour.^{5, 6}

All the preceding results combined to establish the fact that surface nucleation in the recrystallization of aluminium is a reproducible and general phenomenon. Some experiments were next undertaken to determine the cause of this behaviour. As it appeared likely that a surface oxide film might be responsible, one crystal (No. 15) was etched in a hot 10% sodium hydroxide solution for 20 min., and then extended under the etch. This treatment produced no surface nuclei, since further etching after extension did not increase the recrystallized grain-size (samples (a) and (b), Fig. 5, Plate XXVII). Another section of the same crystal was etched in the same reagent for a similar length of time, but was removed from the etch, washed, dried, and allowed to stand in air for 10 min. before being extended. The surface-nucleation effect was then present, as shown by the significant difference between samples (c) and (d) of Fig. 5. This is considered strong evidence for the belief that a surface layer of oxide on the crystals causes the surface-nucleation effect. (The comparatively fine grain-size of all the samples in Fig. 5 is thought to be due to nucleation in the heavy deformation bands formed in crystals with an initial orientation very near $\langle 110 \rangle$.)

The behaviour of some crystals in experiments of this type led to the conclusion that a crystal must remain in the etch for an appreciable period of time before the surface oxide is completely removed. If, for example, a sample was immersed in an etch and pulled immediately, the surface-nucleation effect was not eliminated (samples (a) and (b), crystal No. 14, Fig. 6, Plate XXVII), even though a vigorous reaction occurred. If, however, the crystal remained in the etch for several minutes before it was extended, the surface nucleation became less marked (samples (c) and (d), Fig. 6). The same effect was found in crystal No. 9.

IV.—DISCUSSION

It is well known that an oxide film on the surface of a single crystal can increase its yield stress.^{7, 8} It has recently been shown⁹ that the "abnormal after-effect" in twisted wires, both single-crystal and polycrystalline, can be accounted for on the assumption that dislocations are held up below the surface of a specimen by the presence of an oxide layer, and that removing the oxide allows the dislocations to escape.

Since it is generally agreed that recrystallization nuclei arise in regions of high strain (i.e. high dislocation density), and since the surface-nucleation effect has been found to depend upon the presence of an oxide film at the time of straining, it seems reasonable to assert that dislocations piled up under a surface oxide layer are responsible for the surface-nucleation effect. There is, however, an important difference between the present results and those of Barrett.⁹ In the present work, simply removing the oxide layer, or a minute layer of metal, from the surface, was not sufficient to release the trapped dislocations and eliminate the surface nucleation. It was necessary to remove an appreciable thickness of metal ($> 2.5 \times 10^{-3}$ cm.) before a marked change in the recrystallized grain-size could be observed. This must mean that the dislocations, once initially blocked by the oxide film, are held up by some other mechanism, and so cannot escape when the oxide film is removed.

The following explanation is suggested:

(1) If a crystal is extended under conditions such that no oxide layer is present, there is no sub-surface pile-up, and consequently no surface nucleation is observed. Such a crystal should have a coarser recrystallized grain-size than an identical crystal pulled in air, and this grain-size should not be affected by etching subsequent to the extension. This behaviour is illustrated in Fig. 5 (cf. sample (a) and (b), (c) and (d), and (a) and (c)). Furthermore, such a crystal should presumably have a lower yield stress than a crystal pulled in air, since there is less resistance to the escape of dislocations from the crystal. No comparative stress measurements were made in the present work, but other investigators have found this effect to occur.⁷

(2) If a crystal bearing an oxide layer is extended, dislocations are prevented from escaping from the surface, and consequently dislocations pile up on the active slip planes at the surface. Local stress concentrations result from these dislocations, which may exceed the yield stress of the material in regions just below the surface. Frank-Read sources in other slip planes will then operate to produce a minute network of intersecting planes on which slip has occurred.* This network will presumably extend to a depth beneath the surface roughly equal to the depth of a dislocation pile-up. Although the exact mechanism by which recrystallization nuclei are formed is not known, it is hardly questionable that a region of high

dislocation density and intersecting slip systems will be a region in which nuclei are most likely to arise. On annealing the crystal, therefore, many recrystallized grains will be nucleated in the surface layer, and the recrystallized grain-size as viewed on the surface will be smaller than for a crystal pulled without an oxide coating. Furthermore, these grains will grow from the surface into the centre of the crystal, thus extending the small grain-size from the surface throughout the specimen, provided that the specimen is not very much larger in thickness than the diameter of the recrystallized grains. If the specimen is large, one would expect to find a surface layer of small grains about a central core of larger grains resulting from the "normal" nucleation frequency in regions unaffected by the pile-up of dislocations on the surface.

The depth of the surface-nucleation layer appears from these experiments to be $2.5\text{--}5 \times 10^{-3}$ cm. The applied stress necessary to extend these crystals by 20% is about 2.3×10^2 kg./cm.² (resolved). It is thus possible to calculate the length of the dislocations piled up under the oxide layer from the equation:

$$L = \frac{n\mu b}{\pi k\sigma}$$

where L is the length of the pile-up, n the number of dislocations, μ the shear modulus, b the Burgers vector, k a constant near unity, and σ the applied stress.¹⁰ If we take $n = 5 \times 10^2$ dislocations, $\mu = 0.27 \times 10^6$ kg./cm.², $b = 2.7 \times 10^{-8}$ cm., $k = 1$, and $\sigma = 2.3 \times 10^2$ kg./cm.², we arrive at a value $L = 5 \times 10^{-3}$ cm., which indicates that the proposed explanation is not inconsistent with the observed results.

These experiments suggest that when a single crystal of aluminium is pulled in air, the distribution of dislocations at the surface is not the same as in the interior of the crystal. This affords further evidence that the surface appearance of deformed crystals may not be representative⁸ of the condition of the material below the surface.

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REFERENCES

1. T. J. Tiedema, Dr.Ing. Thesis, Technische Hogeschool, Delft, **1951**; see also W. G. Burgers, *L'État Solide*, (Rep. 9th Solvay Conf., Brussels), **1952**, 73.
2. C. D. Graham, Jr., M.Sc. Thesis, University of Birmingham, **1953**.
3. C. S. Barrett, P. M. Aziz, and I. Markson, *Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197**, 1655.
4. R. J. Stokes, unpublished work.
5. F. D. Rosi and C. H. Mathewson, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, **188**, 1159.
6. N. K. Chen and C. H. Mathewson, *ibid.*, 1951, **191**, 653.
7. E. N. da C. Andrade, *Inst. Metals: Symposium on Properties of Metallic Surfaces*, **1952**, 133.
8. A. F. Brown, *Advances in Physics*, 1952, **1**, 427.
9. C. S. Barrett, *Acta Met.*, 1953, **1**, 2.
10. J. D. Eshelby, F. C. Frank, and F. R. N. Nabarro, *Phil. Mag.*, 1951, [vii], **42**, 351.

THE INFLUENCE OF SUB-STRUCTURE ON THE SLIP OBSERVED IN PURE ALUMINIUM AND SOME ALUMINIUM ALLOYS WHEN SUBJECTED TO FATIGUE STRESSES *

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SYNOPSIS

Observations have been made on the modifying effects of sub-structure on subsequent fatigue deformation at both room and sub-zero temperatures. Sub-structures produced by cold rolling altered completely the appearance of the deformation that was produced by subsequent fatigue stresses. A self-annealing process occurred in cold-rolled pure aluminium when subjected to cyclic stresses.

It is concluded that fatigue stresses, by virtue of their cyclic nature, aid the polygonization process in pure aluminium and in certain aluminium alloys and may produce very sharply defined boundaries by a process of crystallite growth.

I.—INTRODUCTION

AN earlier paper¹ described an investigation into the formation of fatigue cracks in aluminium— $\frac{1}{2}$ % silver alloy by cyclic stressing at room temperature. It was concluded from this work that cyclic stressing induced polygonization and that cracks developed in the regions of crystallites, but it was not possible to establish whether the cracks followed the sub-boundaries. A second paper² described a more detailed investigation into the mechanism of deformation of pure aluminium by cyclic stressing. The present paper deals with the modifying effects of sub-structure on the fatigue behaviour of pure aluminium and some simple alloys. Fatigue tests were carried out at room temperature and -195°C . The effect of small additions of manganese on fatigue behaviour was also studied.

II.—MICROSCOPICAL EXAMINATION

Super-purity aluminium specimens were cold rolled and annealed at 600°C . for 1 hr. to produce a grain-size of the order of 1 mm. dia. The specimens were subjected to reverse bending to produce the characteristic slip striations containing irregular slip bands (Fig. 1, Plate XXVIII). The surfaces were repolished and etched with hydrofluoric acid solution to reveal a system of sub-grain boundaries similar to those observed in earlier work.^{1,2} The specimens were then subjected to further cyclic stressing for a short period and the surfaces re-examined (Fig. 2, Plate XXVIII). Strongly marked sub-boundaries were observed, within which the sub-grains were deformed. Similar specimens which had been heavily cold-rolled,

with no subsequent annealing, were then fatigued in a similar manner. Fig. 3 (Plate XXVIII) shows the surface appearance after fatigue with no subsequent polishing or etching. The deformation has outlined the sub-structure produced by the rolling. In certain regions this outlining is heavier, producing bands where the sub-grains are obviously tilted to different angles. These regions may rise to a height of several microns above the normal surface level of the specimen. Such a region is illustrated in Fig. 4 (Plate XXVIII). It is in these regions that cracks first appeared, and Figs. 5 and 6 (Plate XXVIII) indicate such regions after repolishing and etching. Polygonization, followed by growth of sub-grains, is well advanced in these regions, and further fatigue of such material produces localized deformation within sub-grains (Fig. 7, Plate XXIX).

A number of specimens in both the annealed and cold-rolled condition were then fatigued at low temperatures. Figs. 8 and 9 (Plate XXIX) show the surface of an annealed aluminium specimen fatigued at -195°C . under liquid nitrogen. Although slip or deformation is still concentrated into striations, there is a more marked appearance of a sub-structure, deformation or slip being even more concentrated around sub-boundaries than at room temperature. On repolishing and etching these specimens with 1% HF solution, it was found that crystal breakdown had occurred, but the boundaries were usually less well defined than those produced at room temperature and bore a stricter relationship to the slip directions (Fig. 10, Plate XXIX). It would therefore appear that very little re-arrangement or movement of boundaries had occurred, in contrast to the behaviour at room temperature. The cold-rolled material was subjected to

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similar treatment and corresponding micrographs obtained (Figs. 11 and 12, Plate XXIX, Fig. 11 before, and Fig. 12 after, repolishing and etching). In Fig. 11, it appears that a progressive breakdown of the crystal into smaller crystallites has occurred. Repolishing and etching (Fig. 12, Plate XXIX), did not reveal these smaller grains, but no growth was observed at this temperature, although some of the sub-boundaries became more sharply defined. These observations are summarized in Table I.

TABLE I.—Structure of Pure Aluminium Before and After Fatigue at Room Temperature and -195°C .

	Annealed	Cold Rolled
Initial condition	Large grains.	Small crystallites.
After room-temperature fatigue	Polygonization, cracks starting at regions of breakdown.	Polygonization and growth of crystallites, cracks start in regions of grain growth.
After low-temperature fatigue (-195°C .)	Crystal breakdown, cracks associated with regions of breakdown.	Formation of elongated crystallites, cracks associated with these crystallites.

It has been shown³ that small additions of manganese to pure aluminium increase the recrystallization temperature, and it was therefore considered that they might inhibit or reduce the polygonization and growth of sub-grains which had been observed in cold-rolled pure aluminium subjected to fatigue stresses. An alloy of 1% manganese in aluminium was prepared in the form of a 1.5-in.-dia. billet which was solution-treated for 20 hr. at 630°C . and quenched in cold water. The billet was then cold rolled to a thickness of 0.025 in., and fatigued in the cold-rolled condition at room temperature. Fig. 13 (Plate XXX) shows the surface appearance after fatigue with no subsequent polishing or etching. Deformation has again outlined the sub-structure produced by rolling, but the heavily deformed regions are fewer than those in the pure material (Fig. 3, Plate XXVIII). Subsequent repolishing and etching confirms this observation, and Fig. 14 (Plate XXX) demonstrates the limited extent of the polygonization and growth of sub-grains which occurred in this alloy.

The behaviour of aluminium-1.3% iron, aluminium-5% zinc, and aluminium-2% iron-5% magnesium alloys, when fatigued in the cold-rolled condition at room temperature, was similar to that of pure aluminium and the aluminium-1% manganese alloy. Figs. 15 and 16 (Plate XXX) illustrate the type of deformation produced by fatiguing aluminium-1.3% iron alloy in the annealed and cold-rolled conditions, respectively. Fig. 16 shows clearly outlined sub-boundaries produced by cold rolling and accentuated by fatigue and Figs. 17 and 18 (Plate XXX) show similar effects for aluminium-5% zinc alloy.

III.—ELECTRON-MICROSCOPE EXAMINATION

It has been shown that surface disturbance is concentrated at what appears to be a network of bound-

aries outlining the existing sub-structure in the material. In order to examine the mode of deformation at these boundaries, replicas were taken from the surfaces and examined with the electron microscope. Figs. 19 and 20 (Plate XXX) show typical structures which can be correlated with the optical micrographs. The sub-boundary markings visible in the optical micrographs are seen as heavily ridged contours, representing large local disturbances, and widespread slip is evidently occurring within the sub-grains. This was not resolvable under the optical microscope.

IV.—DISCUSSION

A region of lattice curvature may polygonize with the formation of a sharply defined boundary. If this happens on a prepared surface, a ridge is formed which can be detected microscopically. This ridge is due to recovery of the curvature by the movement

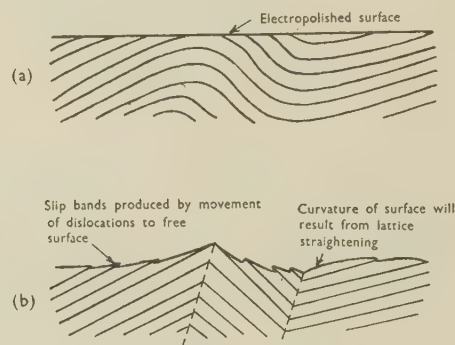


FIG. 21.—Diagram Showing How Surface Tilts May Be Produced by Polygonization. (a) Crystal containing regions of curvature, (b) crystal after polygonization.

of dislocations into arrays, and the effect is to produce surface tilts (Fig. 21).

In pure aluminium these movements of dislocations are accelerated by increase in temperature and also by an applied stress, either static or cyclic. Dislocation arrays will move under the action of a shear stress, sweeping up other dislocations as they move. This will produce boundaries closer in nature to normal grain boundaries, and the normal processes of recrystallization and grain growth will occur.

It would appear that the addition of solute atoms such as manganese to the aluminium lattice reduces the rate at which the dislocation arrays move under the action of a shear stress, and hence also the rate at which recrystallization and grain growth occur.

In cold-rolled aluminium subjected to fatigue, growth of the crystallites occurs in the highly stressed regions, giving rise to larger grains in which further deformation is concentrated. This concentrated deformation results in an eruption of material producing surface irregularities (Fig. 4, Plate XXVIII). Fig. 22 indicates schematically in section the appearance of such an eruption. The fatigue cracks are associated with these eruptions. Fig. 5 (Plate XXVIII) shows a

system of cracks which have occurred within recrystallized regions. These regions are very similar in appearance to the striated structures produced by breakdown and polygonization from the annealed crystals. They differ, however, in the fact that they are not crystallographic, but seem to be oriented with respect to the maximum resolved shear stress, the background structure being an aggregate of small sub-grains produced by the cold rolling. The striations,

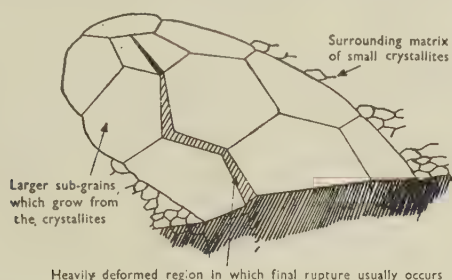


FIG. 22.—Schematic Representation of Region on the Metal Surface where Growth of Sub-Grain has Occurred.

produced by fatiguing the annealed crystals, are regions where slip is concentrated and often exhibit irregularities, which suggests that the slip is influenced by the existence of sub-boundaries. There is also evidence that such striations form ridges on the crystal surface similar in nature to the eruptions described earlier.

It has been suggested by Seitz⁴ and others that an avalanche movement of dislocations will produce a number of vacant lattice sites in the vicinity of slip bands. This high density of vacant lattice sites will lead to greatly increased local rates of self-diffusion, thus aiding the process of recovery and allowing further deformation to occur in these regions.

V.—CONCLUSIONS

(1) Sub-grain boundaries are delineated after a period of cyclic stressing, particularly those parts of the boundaries running parallel to the operative slip direction.

(2) The irregular nature of the slip bands developed

by fatigue stresses, even in annealed material, is thought to be due to residual sub-grain boundaries. Slip bands produced by static stressing do not show this sensitivity to the presence of sub-boundaries.

(3) After fatiguing, the sub-structure produced by cold rolling is almost completely delineated by deformation marks on the metal surface. The deformation marks are heavier in certain regions, thus often producing a banded structure analogous to the striations produced in annealed crystals. This banded structure, however, is determined by the stress directions rather than by any crystallographic considerations.

(4) The cyclic stresses not only produce slip deformation but promote the polygonization process, thus producing surface ridges.

(5) Growth of the sub-grains may occur in cold-rolled aluminium in certain regions when the material is subjected to fatigue stresses. After a period of fatigue stressing these regions were forced up above the general surface level, often by as much as 5μ , and it is in these regions that fatigue cracks occur.

(6) These regions of grain growth seemed to be undergoing continual plastic deformation under the action of the fatigue stresses, even when the surrounding matrix appeared to be unaffected, and they can therefore be considered as soft spots in the material.

(7) A summary is given of the effects of low temperature on the formation of crystallites and crystallite growth in annealed and cold-rolled aluminium.

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REFERENCES

1. P. J. E. Forsyth, *J. Inst. Metals*, 1951–52, **80**, 181.
2. P. J. E. Forsyth, *ibid.*, 1953–54, **82**, 449.
3. R. Chadwick and W. H. L. Hooper, *ibid.*, 1948–49, **75**, 609.
4. F. Seitz, *Advances in Physics*, 1952, **1**, 43.

1584 THE CONSTITUTION OF ALUMINIUM-RICH ALLOYS CONTAINING COPPER, MANGANESE, AND SILICON*

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SYNOPSIS

Constitutional diagrams are presented for the ternary aluminium-manganese-copper system in the range 0-4% manganese and 0-6% copper and also for the 2%- and 1%-manganese levels of the quaternary aluminium-copper-manganese-silicon system in the range 0-5% copper and 0-2% silicon. All diagrams are drawn as a result of micrographic examination of chill-cast specimens annealed for 21 days at 460° C. The metastable *G* phase of the binary aluminium-manganese system occurred in the quaternary alloys, and a fine background precipitate of manganese-containing compounds was also encountered. No quaternary phase is present in the aluminium-rich alloys.

I.—INTRODUCTION

THE present paper describes experiments on the constitution of aluminium-rich alloys containing manganese, copper, and silicon, after annealing for 21 days at 460° C. The major part of the investigation was concerned with the microscopical examination of chill-cast and annealed specimens, although X-ray examination of certain specimens was found useful for distinguishing between the ternary compounds in the quaternary system.

The specimens were made up from the following materials: super-purity aluminium (99.995%); one of three aluminium-manganese master alloys containing, respectively, 5.60, 7.37, and 9.56% manganese, having a super-pure aluminium base; an aluminium-silicon master alloy with a super-pure aluminium base and containing 13.01% silicon and 0.25% iron; and an aluminium-copper master alloy containing 33% copper composed of super-purity aluminium and copper of 99.995% purity.

The alloys were made in the form of ingots weighing 16 g. each, by melting the aluminium in an alumina-lined fireclay crucible in an electric-resistance furnace and adding the desired amounts of manganese, silicon, and copper in the form of master alloys. When the alloy was completely liquid, it was stirred with an alumina rod and immediately cast into a heavy iron mould to produce a fine-grained, chill-cast, ingot $\frac{1}{2}$ in. in dia. A portion of each ingot was enclosed in a sealed evacuated capsule of hard glass, and the capsule annealed for 21 days at $460^{\circ} \pm 2^{\circ}$ C. in a tubular resistance furnace controlled by an Electroflo temperature regulator.

Specimens were prepared for micrographic examination by the usual methods using a metal polish of the "Brasso" type. Critical specimens were analysed

by Messrs. Johnson, Matthey and Co., Ltd., to whom the authors' thanks are due. In the diagrams such specimens are denoted by the symbol *A* placed near the experimental point.

II.—PREVIOUS INVESTIGATIONS

The understanding of equilibrium relations in the aluminium-rich corner of the quaternary system requires a knowledge of the ternary alloy systems of aluminium-copper-silicon, aluminium-manganese-silicon, and aluminium-manganese-copper. Reliable isothermals at 460° C. are fortunately available for the first two systems,^{1,2} and the general form of the aluminium-manganese-copper system^{3,4} is known at about this temperature. It was the availability of this information which determined that the present work should be concerned with the temperature of 460° C.

1. THE SYSTEM ALUMINIUM-COPPER-SILICON

The aluminium-rich portion of this system has been investigated in great detail by Phillips,⁵ who has presented liquidus, solidus, and solid-solubility information for a wide range of aluminium-rich alloys. A much more restricted investigation of the solid-solubility relationships at 460° C. by Axon¹ is in agreement with the solid-solubility results of Phillips⁵ for 450° and 475° C. The phases encountered at the aluminium-rich corner of this system are the solid solution of copper and silicon in aluminium, the binary compound θ of the aluminium-copper binary system, sometimes designated CuAl_2 , and the element silicon. No ternary compounds are encountered.

2. THE SYSTEM ALUMINIUM-MANGANESE-SILICON

The aluminium-rich portion of this system has been studied by Bückle,⁶ by Phillips,⁷ and by Axon and

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Hume-Rothery.² The 460° C. isothermal of Axon and Hume-Rothery² covers the composition range 0–4% manganese and 0–3% silicon, and within this range the following four phases have been reported: the ternary solid solution of manganese and silicon in aluminium; silicon; the binary compound MnAl_6 ; and a ternary compound designated T_{Si} by Axon and Hume-Rothery.² The ternary compound T_{Si} is identical with the compound T of Bückle⁶ or $\alpha(\text{Mn-Si})$ of Phillips.⁷ The same phase has also been designated $c\text{-AlMnSi}$ by Phragmén.⁸ Preliminary experiments on the quaternary system indicated that it would be desirable to recheck the diagram put forward by Axon and Hume-Rothery.²

Consequently a series of 20 ternary alloys were prepared in the composition range 0–2% silicon and 0–3% manganese. These alloys were annealed in vacuum for 21 days at 460° C. and examined microscopically. Although the new experiments confirmed the positions of the phase boundaries proposed by Axon and Hume-Rothery,² a more detailed examination of the specimens revealed two points of interest relating to the distribution of the phases. First, it was observed that in all cases where MnAl_6 was present the annealed specimens contained a proportion of the metastable phase G . This was unexpected in view of the work of Little, Raynor, and Hume-Rothery.^{9, 10} Secondly, it was noted that in addition to the relatively large and easily identifiable crystals of MnAl_6 , G , and T_{Si} , there was a marked spottiness of the aluminium matrix. This background of spots in aluminium alloys containing manganese has been discussed by Dudek, Mahl, and Seemann¹¹ and by Seemann and Dudek,¹² and a good example of the effect is shown in Fig. 2 (a) of the paper by Little, Raynor, and Hume-Rothery.⁹ Dudek and his co-workers^{11, 12} have referred to this fine structural constituent as the U phase.

In the present investigation the fine precipitate was found to occur only in the annealed alloys containing manganese. Thus, binary aluminium-manganese, ternary aluminium-copper-manganese and aluminium-manganese-silicon, and quaternary aluminium-copper-manganese-silicon alloys all showed the fine structure (U phase) after annealing. It was not observed in the aluminium-copper, aluminium-silicon, or aluminium-copper-silicon systems after annealing; moreover, it was never observed in the chill-cast specimens of manganese-containing alloys. It was further noted that a period of 1 hr. at 460° C. was sufficient to produce the fine constituent from the chill-cast specimen but that more prolonged annealing, for periods up to 21 days, had very little effect upon its appearance. The amount in the ternary systems was found to decrease as the manganese content of the alloys was reduced, and the detailed appearance and etching characteristics of this constituent in any particular specimen were found to depend on the exact composition of the specimen in both the ternary and quaternary systems. In the binary aluminium-manganese system it appeared

to behave like a very finely dispersed mixture of MnAl_6 and G . In the ternary systems the fine constituent behaved as a mixture of varying proportions of MnAl_6 , G , and the appropriate ternary phase.

It is very difficult to obtain an unambiguous identification of the individual small particles of the finely dispersed U phase in any particular alloy, but a general review of the evidence suggests that the term U phase is misleading, since more than one crystal type may be involved and, moreover, the crystal types present in the fine constituent of any particular alloy appear similar to those present in a massive form in the same alloy. Thus, it might be convenient to refer to the U phenomenon, rather than the U phase.

In the diagrams which follow it has been assumed that the fine constituent (U phenomenon) in each specimen consists of small particles of those manganese-containing compounds which are present in a massive form in the particular specimen. The reason for the rapid appearance of the fine constituent when the chill-cast specimens are annealed is presumably associated with the ease with which manganese is retained in forced solid solution in chill-cast material. On reheating the ingot, a portion of this manganese precipitates in the finely divided form characteristic of many aluminium-rich alloys containing manganese. A high degree of supersaturation in the chill-cast alloy would be expected to produce precipitation at a large number of sites when it was reheated below the solidus.

Although the fine mode of precipitation in manganese-containing alloys has not hitherto been specifically discussed in connection with purely constitutional investigations, two recent papers by Chadwick, Muir, and Grainger,¹³ and by Harris and Varley,¹⁴ have been devoted to its influence on the mechanical properties of aluminium-rich alloys. In particular, it has been shown that the presence of a fine precipitate of manganese-bearing compound *within* the grains of aluminium-magnesium-silicon alloys may reduce the susceptibility of the alloys to grain-boundary embrittlement. It is probable that such embrittlement is due to the grain-boundary precipitation of Mg_2Si and will be reduced if particles of the fine manganese-containing precipitate act as nuclei for the precipitation of Mg_2Si within the grains instead of at the grain boundaries.

3. THE SYSTEM ALUMINIUM-MANGANESE-COPPER

There appears to be no previous account of equilibrium relations in this system at 460° C.

Day and Phillips⁴ have reported the liquidus and solidus relationships in the aluminium-rich region as a modification of the earlier work of Petri.³ Petri³ also published an isothermal section of the aluminium-rich corner at 500° C., but unfortunately did not give his detailed experimental points. He reported a ternary compound, T which Raynor¹⁵ has suggested may be based on the composition $\text{Cu}_2\text{Mn}_3\text{Al}_{20}$, with a

range of homogeneity. This ternary compound has been designated $\alpha(\text{Cu-Mn})$ by Day and Phillips⁴ and $r\text{-AlCuMn}$ by Phragmén,⁸ who has confirmed the orthorhombic structure proposed by Petri and placed the composition of the phase approximately midway between the limits which he implied.³

Raynor¹⁵ has reported that the solubility of copper in MnAl_6 is about 0.19%, and that of manganese in $\text{CuAl}_2(\theta)$ less than 0.1%, whilst Day and Phillips,⁴ in discussing some of their preliminary results for alloys annealed for an unspecified period at 500° C., remark on the presence of the metastable G phase in this alloy system.

III.—PRESENT INVESTIGATION

1. THE SYSTEM ALUMINIUM-MANGANESE-SILICON

The examination of 20 alloys in the system aluminium-manganese-silicon has confirmed the posi-

2. THE SYSTEM ALUMINIUM-MANGANESE-COPPER

The results of the present investigation into the constitution of the aluminium-rich alloys containing manganese and copper after annealing for 21 days at 460° C., are shown in Fig. 1. In this diagram the symbol M represents MnAl_6 and G existing together, and for any particular alloy the fine constituent (U phenomenon) is regarded as being composed of those manganese-containing phases which exist in a more massive form in that alloy. The ternary phase is designated T_{Cu} , but is identical with the compound designated $\alpha(\text{Cu-Mn})$ by Day and Phillips⁴ and $r\text{-AlCuMn}$ by Phragmén.⁸ In the unetched specimens the crystals of T_{Cu} appeared irregular in outline and of a pink-grey colour. It could easily be distinguished from θ or MnAl_6 in the unetched specimens, and less easily from G . Etching with a reagent of the type proposed by Keller* gave satisfactory differentiation between

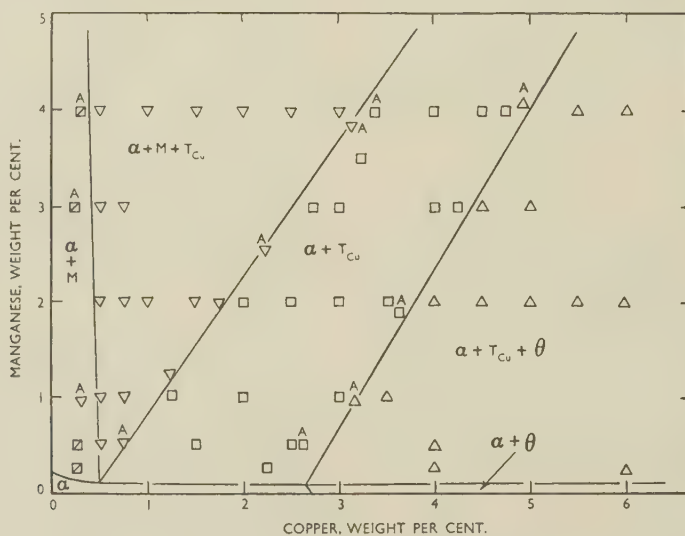


FIG. 1.—Observed Constitution of Chill-Cast Aluminium-Rich Alloys Containing Copper and Manganese, Annealed for 21 Days at 460° C.

KEY.
 \square $\alpha + M$. \square $\alpha + T_{\text{Cu}}$. ∇ $\alpha + T_{\text{Cu}} + M$. \triangle $\alpha + T_{\text{Cu}} + \theta$.

tions of the phase boundaries as determined by Axon and Hume-Rothery.² A more detailed examination showed that the metastable G phase existed in conjunction with MnAl_6 after annealing for 21 days at 460° C. This was found to be a general effect in all the ternary and quaternary alloys, and hence in the present paper the symbol M is used to indicate the presence of MnAl_6 and G existing together in any particular phase field. In view of this co-existence of G and MnAl_6 , it will be appreciated that the diagrams now presented cannot be claimed to be true equilibrium diagrams and must be taken as representing the observed constitution of chill-cast alloys annealed for 21 days at 460° C. The significance of the fine constituent or U phenomenon has already been outlined for this system.

T_{Cu} and G , since the T_{Cu} was etched dark-brown to black, whilst the G was hardly attacked. The phase-field boundaries of Fig. 1 have been drawn after taking into account the relative proportions of the phases present in the alloys, together with the previously reported work of Raynor¹⁵ on the solubility of copper in MnAl_6 and of manganese in θ , and also the composition of the ternary phase, T_{Cu} , as determined by Phragmén.⁸

3. THE SYSTEM ALUMINIUM-COPPER-MANGANESE-SILICON

The constitution of quaternary aluminium-copper-manganese-silicon alloys at 460° C. may be represented by a regular tetrahedron, the faces of which correspond to the 460° C. isotherms of the constituent

* Aqueous solution of 1% HF, 2.5% HNO_3 , 5% HCl.

ternary systems. In the present investigation, restricted to the aluminium-rich corner of the complete tetrahedron, the results are presented in rectangular co-ordinates, so that the aluminium-rich corner of the system may be represented by a rectangular prism. In forming this rectangular prism the aluminium-copper-silicon system is used as the base, since no ternary compound is encountered in this system.^{1, 5}

taining a constant 2% manganese and varying amounts of copper and silicon in the range 0–5% copper and 0–2% silicon, with a less detailed examination of the corresponding section containing 1% manganese. The results for the 2%- and 1%-manganese horizontals are shown in Figs. 2 and 3, respectively. In both these diagrams the points corresponding to the phase boundaries in the ternary

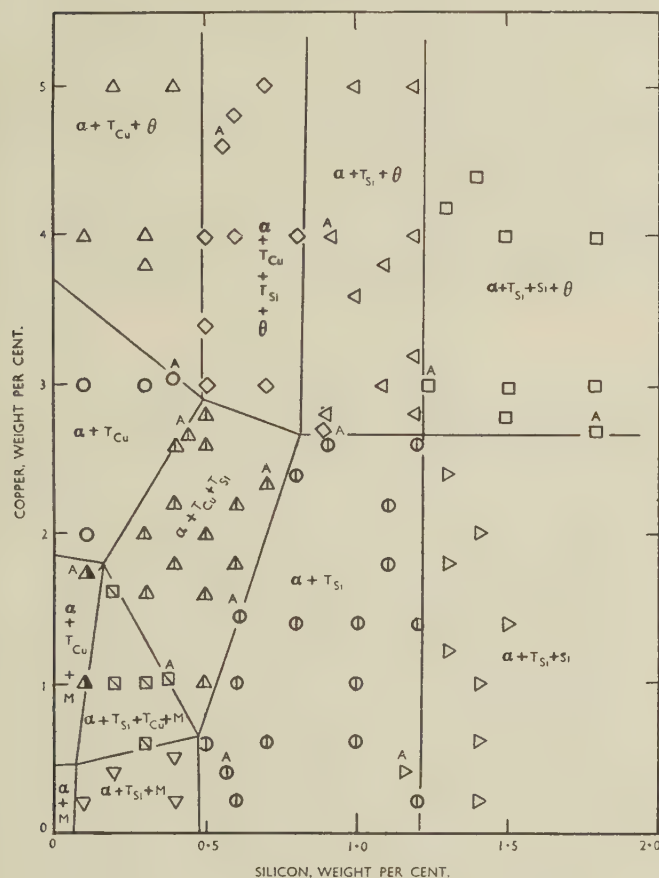


FIG. 2.—Observed Constitution of Chill-Cast Aluminium-Rich Alloys Containing Copper and Silicon and a Constant 2% Manganese, Annealed for 21 Days at 460° C.

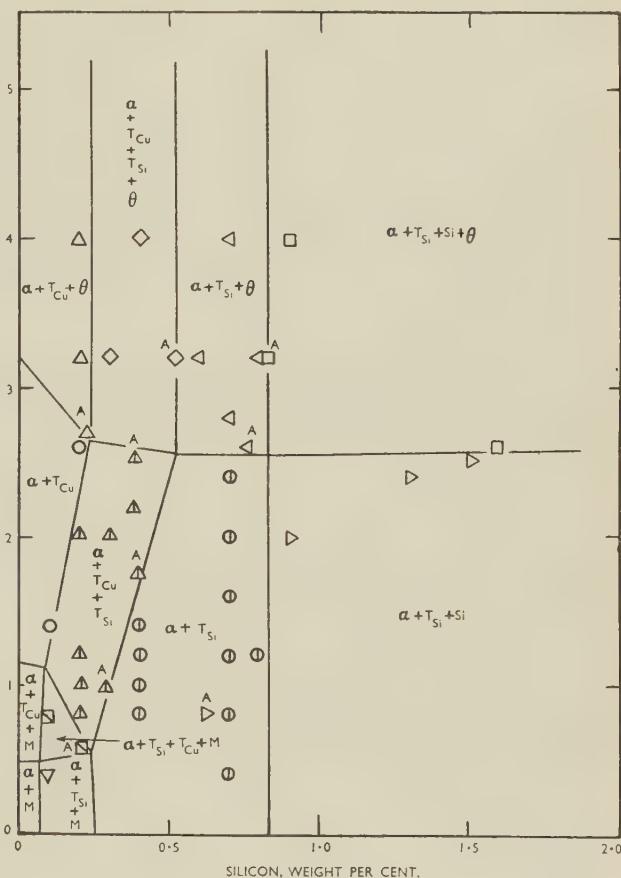


FIG. 3.—Observed Constitution of Chill-Cast Aluminium-Rich Alloys Containing Copper and Silicon and a Constant 1% Manganese, Annealed for 21 Days at 460° C.

KEY TO FIGS. 2 AND 3.

○ $\alpha + T_{Cu}$.
 △ $\alpha + T_{Si} + \theta$.
 □ $\alpha + T_{Si} + Si + \theta$.

⊙ $\alpha + T_{Si}$.
 ▽ $\alpha + T_{Si} + Si$.
 ▢ $\alpha + T_{Cu} + T_{Si} + M$.

▽ $\alpha + T_{Si} + M$.
 ▲ $\alpha + T_{Cu} + M$.
 ◇ $\alpha + T_{Cu} + T_{Si} + \theta$.

△ $\alpha + T_{Cu} + \theta$.
 ▲ $\alpha + T_{Cu} + T_{Si}$.

The two bounding planes of the model are provided by the 460° C. isothermals of the systems aluminium-copper-manganese and aluminium-silicon-manganese; hence in the rectangular model the manganese composition axis is vertical. It will be noted that ternary compounds have been detected in both the aluminium-copper-manganese (T_{Cu}) and aluminium-silicon-manganese (T_{Si}) systems; Phragmén⁸ has reported that the compound T_{Cu} is orthorhombic, whereas T_{Si} is cubic.

The present investigation has been restricted to a detailed examination of the 460° C. isothermal con-

aluminium-silicon-manganese system have been taken from the diagram of Axon and Hume-Rothery,² as checked by the present work, and the points corresponding to the phase boundaries in the ternary aluminium-copper-manganese system have been taken from Fig. 1 of the present paper.

Fig. 2 shows that only those phases previously identified in the ternary systems are found in the aluminium-rich alloys of the quaternary system. As already stated, this figure, which is drawn from the examination of specimens annealed for 21 days at 460° C., is not a true equilibrium diagram, since in all

cases the stable phase MnAl_6 was accompanied by the metastable G phase, and, as before, the two crystal types taken together have been designated M . In addition to the difficulty of identifying the small crystals of the fine constituent in these alloys, a further obstacle was encountered in that the etching characteristics of the ternary phase T_{Si} varied considerably with copper content in the quaternary system. This effect has been noted by Phragmén,⁸ who suggested that the T_{Si} phase took copper into solid solution.

In the present work it was found that in alloys relatively rich in copper the phase T_{Si} approximated in response to the phase T_{Cu} when etched with Keller's reagent, although the T_{Si} crystals tended to darken in a more uneven manner. A more satisfactory distinction between T_{Si} and T_{Cu} in the quaternary alloys was obtained in the unetched condition, when the T_{Si} crystals appeared harder and more in relief than those of T_{Cu} . Additional X-ray evidence was obtained for the presence of T_{Si} in the specimen containing copper 2.6, silicon 0.9, and manganese 2%. This specimen is very near to the copper-rich boundary of the $(\alpha + T_{\text{Si}})$ phase field of Fig. 2, and in etched sections the T_{Si} was difficult to distinguish from T_{Cu} , although a specimen of filings prepared from the alloy showed diffraction lines of T_{Si} .

The corresponding results for quaternary alloys containing 1% manganese are shown in Fig. 3. The general disposition of the phase fields is similar to that in the 2%-manganese section, although the phase fields have, generally speaking, decreased in extent and moved towards the aluminium-rich corner of the diagram. In particular, the four-phase region $(\alpha + M + T_{\text{Cu}} + T_{\text{Si}})$ has become so small that it is difficult to locate the corners of the four-phase triangle accurately by bracketing. Hence, these points in Fig. 3 have been drawn in accordance with the requirement that straight lines through the corresponding corners of the $(\alpha + M + T_{\text{Cu}} + T_{\text{Si}})$ phase fields in Figs. 2 and 3, respectively, must meet just above the horizontal composition plane of the quaternary model. In fact, it has been possible to draw Figs. 2 and 3 so that the intersection takes place at about 0.1% manganese. Similar remarks apply to the three other points in Figs. 2 and 3 at which four separate phase fields come into contact at a point.

ACKNOWLEDGEMENTS

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REFERENCES

1. H. J. Axon, *J. Inst. Metals*, 1952-53, **81**, 209.
2. H. J. Axon and W. Hume-Rothery, *ibid.*, 1948, **74**, 315.
3. H. G. Petri, *Aluminium-Archiv*, 1938, (**14**).
4. (Miss) M. K. B. Day and H. W. L. Phillips, *J. Inst. Metals*, 1948, **74**, 33.
5. H. W. L. Phillips, *ibid.*, 1953-54, **82**, 9.
6. H. Bückle, *Aluminium-Archiv*, 1938, (**13**).
7. H. W. L. Phillips, *J. Inst. Metals*, 1943, **69**, 291.
8. G. Phragmén, *ibid.*, 1950, **77**, 489.
9. (Miss) K. Little, G. V. Raynor, and W. Hume-Rothery, *ibid.*, 1947, **73**, 83.
10. (Miss) K. Little and W. Hume-Rothery, *ibid.*, 1948, **74**, 521.
11. M. Dudek, H. Mahl, and H. J. Seemann, *Metall*, **1948**, (5/6), 75.
12. H. J. Seemann and M. Dudek, *Z. Metallkunde*, 1948, **39**, 319.
13. R. Chadwick, N. B. Muir, and H. B. Grainger, *J. Inst. Metals*, 1953-54, **82**, 75.
14. I. R. Harris and P. C. Varley, *ibid.*, 1953-54, **82**, 379.
15. G. V. Raynor, *ibid.*, 1944, **70**, 531.

A STUDY OF THE BEHAVIOUR OF TITANIUM-RICH ALLOYS IN THE TITANIUM-TIN AND TITANIUM-ALUMINIUM SYSTEMS *

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SYNOPSIS

The hydrogen-pressure method (*J. Inst. Metals*, 1951, **79**, 73) has been used to study the effect of aluminium and tin on the $\alpha \rightleftharpoons \beta$ transformation in titanium. Additions of up to 1 at.-% aluminium have little effect on the transformation, but greater amounts cause a progressive increase in the temperature of the transformation. A slight distortion of the $(\alpha + \beta)$ region at about 3 at.-% aluminium was found. On addition of tin to titanium the transformation temperature is first depressed to a minimum point at 6.5 at.-% tin and $845^\circ \pm 2^\circ \text{C.}$, and thereafter increases with increasing tin concentration. Anomalous relationships between the hydrogen equilibrium pressure and temperature have been observed in the single-phase titanium-tin alloys and between hydrogen equilibrium pressure and hydrogen concentration in α -phase titanium-aluminium alloys.

I.—INTRODUCTION

A LARGE number of elements exhibit a very much greater range of primary solid solubility in β -titanium than in α -titanium. This type of behaviour is very marked in the binary systems of titanium with the transition elements, especially in the systems of titanium with chromium, manganese, iron, cobalt, and nickel,¹ in which there is a remarkable limitation of α -phase solubility, although the β -phase solubility is, in each case, extensive. Since only extremely limited α -phase solubility can be detected in these systems, it is not possible to obtain any experimental results which might suggest a possible cause of such anomalous behaviour. The reason for the existence of extensive α -phase solubility in other titanium-rich systems can, however, be investigated in the hope that a solution of this second problem may contribute towards an understanding of the anomalous behaviour of transition elements of the First Long Period with respect to α -titanium.

The elements which exhibit extensive α -phase solubility in titanium may be divided into two groups, in which the dissolved elements form interstitial and substitutional solid solutions, respectively. The elements which form interstitial solutions in titanium are oxygen, nitrogen, and carbon. The metals of Groups IIIB and IVB of the Periodic Table constitute the second group.

Seybolt² has shown that the maximum solubility of oxygen in α -titanium is consistent with the values of the maximum solubility of oxygen in a number of other transition elements, and that the relative extent of oxygen solubility in the various elements can be directly related to lattice-strain-energy parameters. The range of α -phase solubility of nitrogen and carbon

in titanium and the difference between the extent of the α - and β -phase solid solubilities of oxygen, nitrogen, and carbon in titanium can also be explained largely in terms of strain-energy considerations. Thus an investigation of such systems could not be expected to provide information relevant to the problem of the lack of substitutional solubility of elements of the First Long Period in α -titanium. A study of the second group of α -soluble elements is, therefore, important. The titanium-aluminium and titanium-tin systems were selected for study as representative examples of the effects produced by dissolving elements of Group IIIB and IVB in titanium.

It has previously been shown that additions of aluminium cause a progressive increase in the temperature at which the $\alpha \rightleftharpoons \beta$ transformation in titanium takes place.^{3,4} Conflicting results have, however, been published on the effect of tin on the transformation.^{5,6} In previous work on both systems, few titanium-rich alloys have been examined, and the present investigation was carried out, therefore, in order to determine accurately the form of the $(\alpha + \beta)$ region in the two systems over a limited range of titanium-rich compositions.

II.—PREPARATION OF SPECIMENS

The titanium metal used in the present investigation was prepared by the iodide method (Vickers hardness 70 to 80) and contained about 0.2 at.-% zirconium as the only significant metallic impurity. A hydrogen-pressure investigation of the material showed that the $\alpha \rightleftharpoons \beta$ transformation took place over the temperature range $882^\circ\text{--}879^\circ \text{C.}$ The extent of departure from the isothermal transformation found for the titanium can be accounted for almost com-

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pletely by the effect of the known zirconium content of the metal, and it would appear, therefore, that the starting material contained no significant amount of impurity other than zirconium.

Experimental alloys were prepared, using either aluminium or tin of 99.9% purity, by melting the component metals together in an argon-atmosphere arc furnace. The resulting ingots were forged at 700° C. into bars which, after removal of the contaminated surface, were homogenized for 100 hr. at a temperature of 1000° C. in the case of titanium-aluminium alloys and 940° C. in the case of the titanium-tin alloys. The homogenizing treatment was carried out with the alloys sealed into evacuated silica tubes which were gettered before being placed in the furnace.

III.—EXPERIMENTAL METHOD AND PROCEDURE

The temperature range of the two-phase ($\alpha + \beta$) field was determined for each alloy by the hydrogen-pressure method. In this method, details of which have already been published,⁷ a small quantity of hydrogen amounting to about 0.05 at.-% is dissolved in an alloy specimen contained in an enclosed system, and the equilibrium hydrogen pressure, p , set up is measured as a function of temperature. A linear relationship between $\ln p$ and $1/T$ (where T is the absolute temperature), indicates that the alloy is single-phase. In the two-phase ($\alpha + \beta$) region, the $\ln p/(1/T)$ relation gives a smooth curve.

In previous investigations the direct method of taking successive measurements throughout the whole temperature range of the ($\alpha + \beta$) region, either on cooling or heating, was used. Owing to the fact, however, that the amount of interdiffusion of the component elements of the alloy which must take place before metallurgical equilibrium is attained increases progressively with the amount of the precipitating phase, the method is very slow. In the present investigation a quicker and more accurate method of obtaining the experimental results was adopted.

In determining the $\beta/(\alpha + \beta)$ boundary, the alloy was first heated to a temperature well into the single-phase β region. Hydrogen-pressure readings were then taken at a series of decreasing temperatures until a departure from the hitherto linear $\ln p/(1/T)$ relationship indicated that the specimen had entered the ($\alpha + \beta$) region. The specimen was maintained at this temperature (to within $\pm 0.1^\circ$ C.) until no further change in the hydrogen pressure with time could be detected. The specimen temperature was then decreased by 2° C. and the temperature again held constant until a steady hydrogen pressure was achieved. If the ($\alpha + \beta$) region were sufficiently extensive, at least four equilibrium points lying on a smooth curve could be obtained in this way. The process was then reversed and the temperature increased,

again in steps of 2° C., until the alloy had once more become single-phase. The curves representing the two-phase region were not quite coincident because of a hysteresis effect. Both curves were extrapolated until they intersected the linear $\ln p/(1/T)$ curve of the β -phase. In general, the temperature difference between the two points of intersection was about 3° C. The mean value was taken to be the most probable value of the temperature of the $\beta/(\alpha + \beta)$ boundary. The $\alpha/(\alpha + \beta)$ boundary was obtained in a similar way.

IV.—EXPERIMENTAL RESULTS

1. TITANIUM-ALUMINIUM SYSTEM

The partial constitutional diagram obtained by plotting the mean value of the $\beta/(\alpha + \beta)$ and $\alpha/(\alpha + \beta)$ boundaries obtained from the hydrogen-pressure/temperature curves of a series of titanium-aluminium

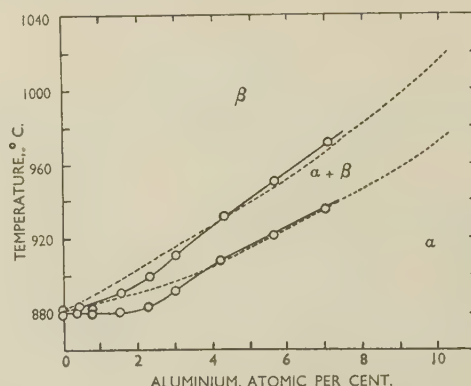


FIG. 1.—The Effect of Aluminium on the $\alpha \rightleftharpoons \beta$ Transformation in Titanium. The broken lines are the boundaries of the ($\alpha + \beta$) region reported by Bumps, Kessler, and Hansen.³

alloys is given in Fig. 1. The results of Bumps, Kessler, and Hansen,³ obtained by metallographic examination of quenched alloys, are also included in the diagram for comparison.

The hydrogen-pressure curves of an alloy containing 0.78 at.-% aluminium indicated that the $\alpha \rightleftharpoons \beta$ transformation occurred almost isothermally, whereas the 0.40 at.-% aluminium alloy had an ($\alpha + \beta$) region which extended over a temperature range of about 5° C. Since the experimental error in the determination of the phase boundaries in this investigation is about 2° C., it is not possible to decide from the present results whether or not a minimum point exists at about 1 at.-% aluminium. In drawing the $\beta/(\alpha + \beta)$ boundary (Fig. 1) it has been assumed that the effect is due to experimental errors. It would be necessary to obtain titanium of at least 99.99% purity before attempting to decide between the two possibilities. There is an excellent agreement between the present results and those of Bumps, *et al.*, in all alloys containing more than 4 at.-% aluminium. Below this amount of aluminium, the form of the ($\alpha + \beta$)

region obtained in the present investigation differs from that given by the earlier workers. It must be pointed out, however, that Bumps, *et al.*, examined alloys only at 900° C. in this composition range and that their findings at this temperature are entirely consistent with the present more detailed results.

Between 2 and 4 at.-% aluminium the $\beta/(\alpha + \beta)$ and $\alpha/(\alpha + \beta)$ boundaries show a change in curvature which suggests that either the α - or the β -phase undergoes a change in thermodynamic stability in this composition range. It is not possible from the constitutional diagram to decide which phase is responsible for the slight irregularity in the form of the $(\alpha + \beta)$ region. The change in heat of solution, Q , of hydrogen in the α - and β -phases of the alloys has, therefore, been calculated from the slopes of the experimentally determined $\ln p/(1/T)$ curves in order to detect any anomalous effects in the relationship between Q and alloy composition in the range 2–4 at.-% aluminium. It was found that, below 3 at.-% aluminium, the values of Q obtained from $\ln p/(1/T)$ curves of α -phase alloys were abnormally sensitive to the hydrogen content of the alloys. This hydrogen sensitivity of low-aluminium α -phase alloys gave rise to a scattering of the values of Q obtained for these alloys of the order of 0.5 kg.cal./mole of hydrogen, the scatter being about 2% of the magnitude of the heat of solution in α -phase alloys. At higher aluminium contents the values of Q were no longer sensitive to hydrogen content, and were found to decrease linearly at a rate of 0.70 kg.cal./mole of hydrogen for one atomic per cent. increase in aluminium content. It would appear, therefore, that there is some evidence for attributing the change in curvature of the $(\alpha + \beta)$ region boundaries to a very small change in the stability of the α -phase at a composition between 2 and 4 at.-% aluminium. It is intended to investigate the effect of hydrogen concentration on the heat of solution of hydrogen in titanium-rich titanium-aluminium alloys more fully at a later date.

2. TITANIUM-TIN SYSTEM

In its general form, the $(\alpha + \beta)$ region of the titanium-tin system derived from hydrogen-pressure determinations, which is shown in Fig. 2, resembles that given by Worner.⁵ A minimum point in the $(\alpha + \beta)$ field was found at 6.5 at.-% tin and $845^\circ \pm 2^\circ$ C. No trace was, however, found of a discontinuity due to the peritectoid horizontal reported by Worner to occur at 885° C. in alloys containing more than 8 at.-% tin. The alloys appeared to be β -phase at this temperature. The rate of attainment of metallurgical equilibrium in alloys of higher tin content was found to be slow, and it is possible that the peritectoid reaction had not occurred after a period of 16 hr. at 880° C. Worner, however, used annealing times of only 5 hr. in this temperature range, and there exists, therefore, a fundamental disagreement between the two sets of results on this point.

Anomalous deviations from the linear $\ln p/(1/T)$

curves occurred in both α - and β -phase titanium-tin alloys. In β -phase alloys containing between 3.5 and 8 at.-% tin, the values of the hydrogen equilibrium pressure at temperatures above 960° C. were smaller than expected by an amount which increased with increasing temperature. As the hydrogen-pressure apparatus was designed to operate only up to 1000° C., this anomalous behaviour could not be fully investigated by this means. Positive deviations from a linear $\ln p/(1/T)$ relationship were found in α -phase alloys at temperatures below 700° C. The deviations became progressively greater as the temperature of the alloy decreased until, at a certain temperature depending on the tin content, the specimen exhibited an isothermal increase in hydrogen

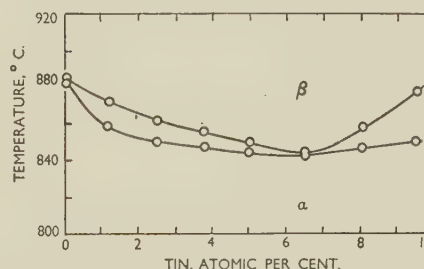


FIG. 2.—The Effect of Tin on the $\alpha \rightleftharpoons \beta$ Transformation in Titanium.

pressure which continued until the greater part of the hydrogen initially dissolved in the specimen was expelled. The temperature at which the hydrogen was expelled increased from 640° C. in a 2.5 at.-% tin alloy to 690° C. in a 9.5 at.-% tin alloy. Microscopic examination of alloy specimens containing no hydrogen, which had been maintained for periods of up to 100 hr. at temperatures below that at which the hydrogen pressure had increased isothermally, showed no evidence of more than one phase.

The change in resistivity with temperature of a hydrogen-free titanium-4 at.-% tin alloy was measured in the α - and β -phase regions. In each region the resistivity/temperature curve showed no discontinuity in slope. It would seem therefore that the anomalous hydrogen-pressure/temperature effects in the β -phase at high temperatures and in the α -phase at low temperatures must be attributed to the presence of hydrogen in the alloy specimens.

V.—DISCUSSION

Although large additions of aluminium to titanium cause the $\alpha \rightleftharpoons \beta$ transformation to occur at higher temperatures than in the pure metal, the first additions of aluminium do not greatly increase the transformation temperature. Tin causes an initial depression of the transformation. It would appear, therefore, that the α -phase attains greater stability with respect to the β -phase only after approximately 2 at.-% aluminium or 6.5 at.-% tin has been dissolved in it.

It is possible that the anomalous changes in the

heat of solution, Q , of hydrogen in α -phase titanium-aluminium alloys at about 3 at.-% aluminium are due to a Brillouin-zone-overlap effect. The outer Brillouin zones of a hexagonal lattice have been shown⁸ to have a complicated form, and electrons with energies corresponding to the top of the Fermi surface will, therefore, interact with the lattice in a complex manner. The resulting free-energy changes of titanium solid solutions as a function of electron/atom ratio would probably be small. Hydrogen forms an interstitial solution in titanium, and hence additions of hydrogen will increase the number of free electrons in the metal by an amount which will most probably be less than the number of hydrogen atoms in solution, since it is unlikely that the proton from the hydrogen atom will be unshielded when in the lattice. If the aluminium content of a titanium alloy is such that a zone effect due to a particular electron/atom ratio is occurring, then the change in this ratio due to added hydrogen could readily bring about a variation in Q of the order of magnitude found in these experiments.

In the titanium-aluminium system, the primary α -phase solid solution ends at 36 at.-% aluminium with the appearance of an ordered face-centred tetragonal phase. Pietrokowsky⁹ and Worner⁵ have both shown, however, that a titanium alloy containing 25 at.-% tin has a structure isomorphous with Mg_3Cd . The unit cell of this structure with an ordered arrangement of the tin and titanium atoms may be considered as being made up of four unit cells of the hexagonal titanium lattice. Although aluminium has a smaller, and tin a larger, atomic size than titanium, the solution of both elements in α -titanium causes an increase in the c/a ratio of the hexagonal lattice.^{5, 10} In the solid-solution range, tin is almost twice as effective as aluminium in increasing the c/a ratio. Furthermore,

if the Ti_3Sn structure reported by Pietrokowsky is considered as an ordered solid solution of tin in α -titanium, the c/a ratio of the four component hexagonal close-packed unit cells which combine to form the unit cell of the ordered structure is 1.61, a value which is consistent with the increase in c/a ratio with tin content in the primary α -phase solid solution derived from the parameter measurements given by Worner. It would appear, therefore, that factors affecting the c/a ratio of hexagonal α -titanium may also be contributing to the stability of this structure.

The determination of the effect of aluminium and tin on the $\alpha \rightleftharpoons \beta$ transformation in titanium has brought to light a number of effects which require explanation. It would seem, however, that the cause of these effects can be found only by examining the physical properties of the α - and β -phase solid solutions of aluminium and tin in titanium. Investigations are therefore being carried out on the electrical-resistivity/composition relationships in the primary solid-solution regions and also on the change in heat of solution of hydrogen in titanium with concentration both of dissolved hydrogen and metallic addition elements. Precision lattice-parameter measurements on α -phase solutions would seem to be a fruitful field for further research. At present, however, it is still not possible to give any reason for the extensive solubility of aluminium and tin in α -titanium, and hence no possible cause of the restricted solubility of transition elements of the First Long Period in α -titanium can be suggested.

ACKNOWLEDGEMENTS

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REFERENCES

1. A. D. McQuillan, *J. Inst. Metals*, 1951-52, **80**, 363.
2. A. U. Seybolt and R. L. Fullman, *Trans. Amer. Inst. Min. Met. Eng.*, 1954, **200**, (5), 548.
3. E. S. Bumps, H. D. Kessler, and M. Hansen, *ibid.*, 1952, **194**, 609.
4. H. R. Ogden, D. J. Maykuth, W. L. Finlay, and R. I. Jaffee, *ibid.*, 1951, **191**, 1150.
5. H. W. Worner, *J. Inst. Metals*, 1952-53, **81**, 521.
6. W. L. Finlay, R. I. Jaffee, R. W. Parcel, and R. C. Durstein, *J. Metals*, 1954, **6**, (1), 25.
7. A. D. McQuillan, *J. Inst. Metals*, 1951, **79**, 73.
8. R. L. Berry, M. B. Waldron, and G. V. Raynor, *Research*, 1950, **3**, 195.
9. J. F. Nicholas, *Proc. Phys. Soc.*, 1951, [B], **64**, 953.
10. P. Pietrokowsky, *Trans. Amer. Inst. Min. Met. Eng.*, 1952, **194**, 211.
11. W. Rostoker, *ibid.*, 1952, **194**, 212.

AN ATTEMPT TO SEPARATE TITANIUM FROM OXYGEN BY VACUUM SUBLIMATION, AND SOME MEASUREMENTS OF EVAPORATION RATES*

1586

By A. B. OSBORN,† B.Sc.

SYNOPSIS

Titanium samples containing 2, 6, and 16 wt.-% oxygen were prepared. Each sample was heated *in vacuo* until it evaporated freely, at 1500°–1600° C. The vapour was condensed and examined for oxygen. In each case, the sublimate contained substantially less oxygen than the alloy from which it was evaporated. This process is unattractive for the industrial purification of titanium, since it requires an excessive use of electrical energy.

The evaporation rate, at 1530° C., of titanium containing 6 wt.-% oxygen was found to be approximately equal to the published rate (Carpenter and Mair, *Proc. Phys. Soc.*, 1951, [B], 64, 57) for pure titanium, but from the sample containing 16 wt.-% oxygen, evaporation proceeded at about one-seventh of the normal rate.

Titanium containing 6.25 wt.-% oxygen had previously been reported (Ehrlich, *Z. anorg. Chem.*, 1941, 247, 53) to be much more volatile than other titanium–oxygen alloys. This report was not confirmed.

I.—THE SEPARATION OF TITANIUM FROM OXYGEN

1. INTRODUCTION

ONE of the main problems in the production and refining of titanium is removal of oxygen. If a convenient means were available for removing residual oxygen from titanium, it might enable cheaper production methods to be used. It would also help to solve the problem of utilizing partly oxidized scrap titanium. In spite of obvious difficulties, the process of “vacuum sublimation” was studied to see whether it could be used to separate titanium from oxygen.

2. EXPERIMENTAL TECHNIQUE

A bar of titanium, containing oxygen in homogeneous solid solution, was heated *in vacuo* until it evaporated freely. The vapour was condensed, and when sufficient had been collected, it was examined for oxygen content, and compared with the original titanium sample. The results indicated the extent to which titanium and oxygen had been separated by vacuum sublimation.

(a) Procedure

Samples of titanium alloyed with 2, 6, and 16 wt.-% oxygen were prepared. At 1500° C. the phases present in these alloys should be $\alpha + \beta$, α , and $\alpha + \text{TiO}$, respectively. The samples were formed into bars 1 cm. in dia. and 12 cm. long. Each bar in turn was mounted in an apparatus in which it was heated *in vacuo*, by passing alternating current through the bar. This method avoided any risk of contamination

which might have been caused by heating in a crucible. During heating, the bar was surrounded by a cylinder of titanium foil, which remained cool enough to condense and collect the sublimate.

When sufficient sublimate (about 2 g.) had been de-

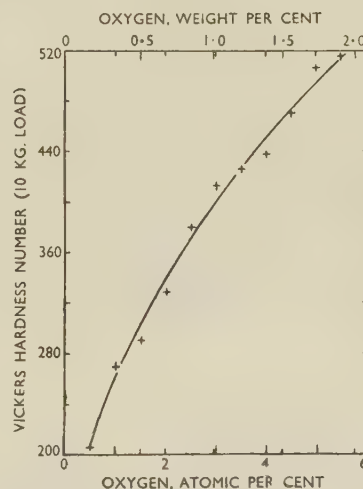


FIG. 1.—Hardness/Oxygen-Concentration Relationship for Annealed Titanium–Oxygen Alloys. (After Jenkins and Worner.¹)

posited, the coated foil was removed from the apparatus, cut into strips, and melted in an argon-arc furnace to form a button. Hardness measurements were made on the vertical section obtained by sawing the button in half. The oxygen content was estimated from the hardness curve (Fig. 1) published by Jenkins and Worner.¹

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Hardness measurements were used for assessing the oxygen content of titanium samples because reliable analytical methods were not readily available. This method depends on the assumption that any other impurities in the samples would make them harder, not softer. Consequently the hardness values were taken to indicate the maximum possible amount of oxygen present in any sample.

(b) Apparatus

The evaporation chamber is illustrated in Fig. 2. It consisted of a brass top plate, sealed by an O-ring to a Pyrex cylinder. An outer bell jar, not shown, provided water-bath cooling for the Pyrex cylinder.

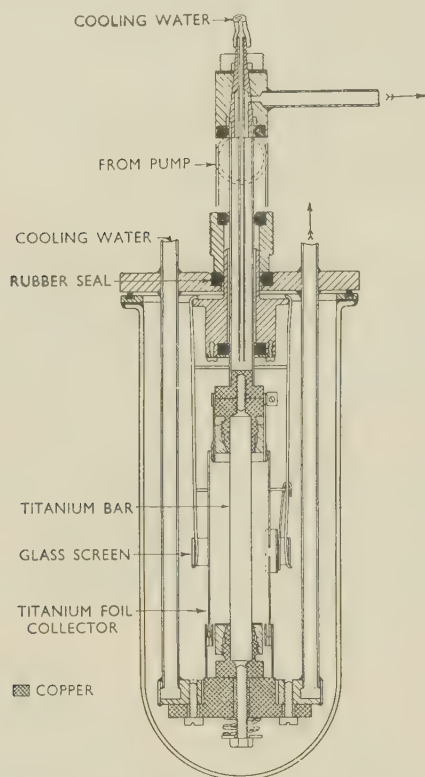


FIG. 2.—Diagram of Evaporation Chamber.

Small copper chucks were used to hold the titanium bar and conduct the heating current into it. These were connected to a variable transformer by water-cooled copper tubing. Thermal expansion of the titanium bar was accommodated by vertical movement of the top contact, through vacuum-tight seals.

The temperature reached by the middle part of the bar was measured with an optical pyrometer. For this purpose, a 5-mm. hole was drilled through each titanium foil collector. Level with this hole a cylindrical glass screen was mounted in such a way that it could be rotated without affecting the vacuum. A clean area of glass was brought in front of the hole whenever a temperature reading was made.

An oil diffusion pump was used to evacuate the

apparatus, and it maintained a pressure of less than 4×10^{-4} mm. Hg during the evaporation process.

(c) Preparation of Alloy Bars

The titanium alloy containing 2% oxygen was prepared in an argon-arc furnace by melting together the appropriate mixture of titanium sponge and titanium dioxide powder. A sample of the sponge used for all the alloys analysed after arc-melting as follows: silicon 0.8, manganese 0.005, copper 0.002, iron 0.01, magnesium 0.00, tungsten 0.03, and carbon 0.04%, with D.P.N. = 176.

The oxide powder was of laboratory reagent grade, containing about 4% moisture, and traces of iron, calcium, and phosphate. The ingot was remelted three times to ensure homogeneity. It was then made into a bar by hot forging. Finally, the oxide skin and surface layers of metal were machined off to a depth of about 3 mm., and hardness measurements were made to check the composition.

The alloy containing 6% oxygen could not be forged, so a powder process was used. The required mixture of titanium sponge and oxide was melted in the arc furnace, then crushed in a percussion mortar to pass 100 mesh. The resulting powder was pressed dry, to form a rectangular compact, then sintered *in vacuo* for 1 hr. at 1000° C. After turning down to a bar of 12 mm. dia., it was re-sintered at 1250° C. for 3 hr. Final turning to 1 cm. dia. was done with a carbide-tipped tool. This was only possible because the metal was not fully sintered, having only 66% of the theoretical density. The composition of the finished bar could not be checked by hardness measurement in this case, but subsequent X-ray examination suggested a value of 6 ± 1 wt.-% oxygen.

The 16% alloy was made similarly, except that it was necessary to sinter the compact for 3 hr. at 1380° C. before it was strong enough for turning. After two further periods of 15 min. at 1485° C., it was turned to final diameter. The 16% alloy made in this way had about 70% of the theoretical density. It was extremely brittle, and several attempts were made before a bar was obtained which survived long enough for the sublimation experiment to be completed. X-ray examination suggested a composition of 16 ± 2 wt.-% oxygen.

(d) Preparation of Foil Collectors

Using the same stock of material as for the alloy bars, 35 g. of titanium sponge was arc-melted to form an ingot. This ingot, having a D.P.N. = 180, was worked into a strip by hot forging and rolling. After thorough cleaning, the strip was rolled down to foil of 0.05 mm. thickness. Although vacuum-annealing was used, some contamination evidently occurred, since the finished foil, after arc-melting, had a D.P.N. = 284. From the foil, hollow cylinders 8.5 cm. long and 3 cm. in dia. were made by spot welding. During use, each collector was fitted into the top of a cylindrical molybdenum support, which held it in position co-axially with the titanium bar.

3. RESULTS

(a) *Oxygen Content of Sublimates*

The first alloy bar, containing 2% oxygen, showed a D.P.N. = 530. The sublimate from this bar, melted with the foil, produced a button of D.P.N. = 270. This corresponds to an upper limit of 0.6% oxygen in the sublimate. Details for the 2%, 6%, and 16% alloys are given in Table I.

TABLE I.—*Oxygen Content of Sublimates.*

Titanium Alloy Bar	Weight of Sublimate, g.	Weight of Foil, g.	D.P.N. of Button (Foil + Sublimate)	Estimated Upper Limit of Oxygen in Sublimate, %
Ti + 2% Oxygen (nominal) . . .	3.6	1.7	272	0.6
Ti + 6% Oxygen (nominal) . . .	2.0	1.7	315	1.0
Ti + 16% Oxygen (nominal) . . .	1.6	1.8	569	5.1 *

* The last figure in the fifth column (5.1%) was obtained by extrapolation of the curve in Fig. 1. The D.P.N. value, 569, was estimated to correspond to an oxygen content of 2.4 wt.-%.

Each figure given in the fifth column was calculated from the hardness value of the fourth column by assuming that the contamination of the titanium forming the button was due entirely to oxygen in the sublimate. Since the foil was known to contain some impurity, the true figures for oxygen in the sublimates were actually somewhat less than those shown in the fifth column.

A temperature of nearly 1600° C. was needed to obtain adequate evaporation from the 16% alloy. For the other alloys, a temperature of about 1500° C. was used for sublimation.

(b) *Consideration of Results*

The figures given in Table I show that each sublimate contained appreciably less oxygen than the titanium alloy bar from which it was evaporated. It must be concluded that a majority of the oxygen atoms were retained by the lattice during preferential evaporation of the titanium atoms.

It is almost certain that any oxygen atoms which did evaporate would have been held by the collector, since the system was almost closed, and conditions were ideal for "gettering" by the condensed titanium. (The temperature of the collector and deposit was about 1000° C. during the evaporation process.)

Preferential evaporation of titanium would, by itself, have led to a rapid increase in the concentration of oxygen on the evaporating surface. This increased concentration was presumably limited by rapid diffusion of oxygen away from the surface into the bulk of the alloy. Such diffusion could not cause any appreciable change in the bulk composition, as less than 10% of the solid was evaporated in these experiments.

4. CONCLUSION

Appreciable separation of titanium from oxygen has been demonstrated. The practical value of the process, as a means of purification, depends on the rate at which it proceeds. Measurements of the evaporation rate of the 6% alloy described in Part II show that the purification of 1 lb. of titanium in the experimental apparatus would require about 1600 kWh. of electrical energy. It is unlikely that improvements in the thermal efficiency of the apparatus could reduce this to much less than 800 kWh./lb. It is therefore improbable that an economic method of industrial purification could be based on vacuum sublimation.

II.—THE EVAPORATION RATE OF TITANIUM-OXYGEN ALLOYS

1. INTRODUCTION

Published data exist for the evaporation rate of pure titanium and its variation with temperature.² The only known reference to the evaporation rates of titanium-oxygen alloys is the description given by Ehrlich³ of some experiments in which various alloys were heated in an evacuated silica tube.

2. EXPERIMENTAL PROCEDURE

The apparatus described in Part I was used to measure the evaporation rates of the alloys studied.

Each foil collector had a central hole, 5 mm. in dia., for pyrometry. Through this hole the vapour from the titanium alloy bar was able to pass. To measure the evaporation rate of the alloy, a separate slip of foil was mounted close to the hole, so that the emergent vapour condensed and collected on it. The increase in weight of the foil slip was thus equal to the weight of material condensed on an area of the collector corresponding to the hole. Assuming uniform temperature conditions near the centre of the bar, the evaporation rate in this region was calculated from the weight of sublimate.

The surface temperature half-way up the bar was measured with an optical pyrometer, the slip of foil being rotated clear of the hole while the reading was taken. Absorption by the water bath and the various glass surfaces was measured by a subsidiary experiment, and due allowance made when estimating the evaporation temperature.

After the evaporation measurements had been completed, the 16% oxygen bar was drilled for a check on emissivity, and a value of $\epsilon = 0.7$ was obtained for $\lambda = 0.65 \mu$. Since the emissivity of pure titanium is 0.5, the intermediate value of $\epsilon = 0.6$ was chosen for correcting the temperature of the 6% oxygen bar in Table II.

3. RESULTS

(a) *Evaporation Rates*

Table II shows the estimated evaporation rates obtained.

Diameter of hole through which vapour emerged
= 5.16 mm.

Diameter of collector cylinder, in which hole
was drilled = 3.0 cm.

Diameter of alloy bar (evaporating surface)
= 1 cm.

∴ Evaporating area corresponding to the amount
of deposit = $\frac{1}{3} \cdot \pi \left(\frac{5.16}{20} \right)^2 \text{ cm.}^2$

° This area was used in calculating the evaporation rates in the fourth column of Table II.

TABLE II.—*Evaporation Rates.*

Titanium Alloy	Dura- tion of Run, hr.	Weight of Deposit, mg.	Estimated Evaporation Rate in g./cm. ² /sec.	Pyro- meter Read- ing, °C.	ε *	True Temp., °C.
Ti + 6% oxygen (nominal)	3 6	2.4 8.4	3.2×10^{-8} 5.6×10^{-8}	1370 1410	0.6 0.6	1490 1530
Ti + 16% oxy- gen (nominal)	6	3.7	2.5×10^{-8}	1490	0.7	1600
Pure Ti (calcu- lated from pub- lished data)	2.6×10^{-8} 5.4×10^{-8} 16.0×10^{-8}	1490 1530 1600

* ε = Value of emissivity used in calculating true temperature.

No measurements were made on the 2% oxygen alloy, as the bar was distorted by the sublimation experiments.

4. CONSIDERATION OF RESULTS

The temperatures shown in the seventh column of Table II may be in error by $\pm 30^\circ \text{C.}$, owing to uncertainty regarding the effective emissivity and absorption corrections. In spite of this uncertainty, the results show that the evaporation rate of the 6% alloy is of the same order as that of pure titanium. The rate for the 16% alloy is appreciably lower, being perhaps about one-seventh of that for pure titanium.

These results do not agree with those of Ehrlich,³ in which $\text{TiO}_{0.2}$ was said to be considerably more volatile than the other materials tested ($\text{TiO}_{0.1}$, $\text{TiO}_{0.7}$, and pure Ti). Further evidence on this point is given in the following section.

5. THE VOLATILITY OF $\text{TiO}_{0.2}$

When Ehrlich³ heated $\text{TiO}_{0.2}$ in an evacuated silica tube for 36 hr. at 1060°C. , he obtained a deposit, metallic in appearance, on the wall of the tube.

The 6% oxygen alloy used in the present work is not very different in composition from $\text{TiO}_{0.2}$. At 1530°C. it had an evaporation rate similar to that of pure titanium. If it followed the same temperature law as titanium, the volatility at 1060°C. would be negligible (about $0.4 \times 10^{-10} \text{ g./cm.}^2/\text{hr.}$).

To obtain a direct check on the volatility of the 6% oxygen alloy at 1060°C. , an experiment was performed, using a heating process similar to that employed by Ehrlich. Two crucibles were used, one of alumina, the other of zirconia. After heating in air for 1 hr., they were cooled and weighed (see Table III). They were then heated *in vacuo* for 6 hr. at 1100°C. After cooling, the weights were found to be slightly less than before, possibly owing to reduction of trade-marking material. About 2 g. of the powdered 6% oxygen alloy was then weighed in each crucible. Carefully supported in a covered molybdenum boat, the crucibles were placed in a mullite furnace tube. An oil diffusion pump was used to evacuate the tube continuously while it was heated to 1060°C. and maintained at that temperature for 36 hr. After cooling, the crucibles and contents were again weighed. The zirconia crucible and contents showed no change of weight whatever. The alumina one showed a gain of 0.0010 g.

TABLE III.—*Non-Volatility of Titanium + 6% Oxygen at 1060°C.*

	Crucible	
	Alumina.	Zirconia.
Weight * of crucible after heating in air	g. 7.7299	g. 10.1036
Weight of crucible after heating <i>in vacuo</i> for 6 hr. at 1100°C.	7.7282	10.0902
Weight of crucible + powdered alloy	9.9970	11.9899
Weight of crucible + alloy contents after 36 hr. at 1060°C. <i>in vacuo</i>	9.9980	11.9899

* Limit of experimental error on weighings = $\pm 0.0002 \text{ g.}$

From these results it is evident that the 6% alloy is not volatile at 1060°C. It seems probable that the sublimate obtained by Ehrlich³ from $\text{TiO}_{0.2}$, at 1060°C. , was due to some form of contamination, and is not characteristic of the pure titanium-oxygen alloy.

ACKNOWLEDGEMENTS

The author wishes to acknowledge the invaluable help of his colleagues at the Royal Aircraft Establishment. Acknowledgement is also made to the Chief Scientist, Ministry of Supply and the Controller, H.M.S.O., for permission to publish this paper.

REFERENCES

1. A. E. Jenkins and H. W. Worner, *J. Inst. Metals*, 1951–52, **80**, 157.
2. L. G. Carpenter and W. N. Mair, *Proc. Phys. Soc.*, 1951, [B], **64**, 57.
3. P. Ehrlich, *Z. anorg. Chem.*, 1941, **247**, 53.

By D. SUMMERS-SMITH,† B.Sc., Ph.D., A.R.T.C., MEMBER

SYNOPSIS

The solubility of vanadium in gold has been determined by X-ray methods. The maximum solubility is 17.5 at.-% at 970° C., falling to about 13 at.-% at room temperature. A "metallic valency" of 3 for vanadium in solution in gold has been derived from the solubility.

I.—INTRODUCTION

AN estimation of the metallic valencies of the transition metals, when dissolved in gold, has been made recently.¹ This was based on the assumption that the solubility is limited by the electron concentration in a similar way to that of the normal metals in gold, as found by Owen and Roberts.² It was shown that the Group IVA elements titanium and zirconium and the Group VIA element molybdenum exhibited their group valency. Chromium, on the other hand, and the remaining members of the first transition period all showed low valencies of 2 or less. No information was available on the solubility of vanadium, and this has now been examined so that an estimation of its "valency" in solution in gold might be made.

II.—RESULTS

The alloys were prepared from gold and vanadium of 99.9 and 99.4% purity, respectively. Appropriate quantities of the metals were sealed off in evacuated silica tubes and heated for 2 hr. at 1200° C. with continuous shaking. After heating, the tube was quenched in water. The composition of the alloys was calculated from the initial weights of the metals. In no case did the change of weight on melting amount to as much as a change of 0.1 at.-% in the vanadium content. Subsequent heat-treatments of filings from the ingots were carried out in evacuated silica tubes in wire-wound tubular furnaces, controlled to $\pm 1^\circ$ C. Annealing times were extended until measurement of the lattice parameter of the gold solid solution showed no further change. The longest annealing time used was 144 hr. at 500° C.

X-ray powder photographs were taken in a 9-cm. "Unicam" camera, and lattice parameters of the gold solution were calculated, using Nelson and Riley's extrapolation.³ The results are given in Fig. 1, and from this the solubilities at five temperatures have been read off and incorporated in Fig. 2, which shows the limits of the gold-rich solid solution. Extrapolation of the results in Fig. 2 indicates a maximum solubility of 17.5 at.-% vanadium at about 970° C.;

the solubility falls to about 13 at.-% at room temperature.

III.—DISCUSSION

As shown in a previous paper,¹ metallic valencies can be allotted to the transition elements if it is assumed that their maximum solubility in gold is

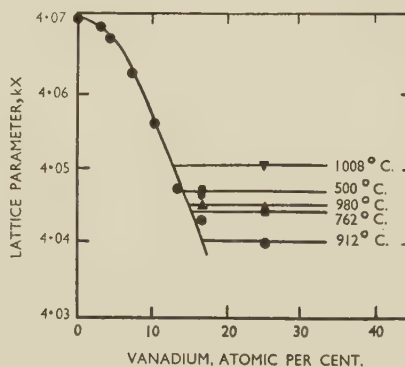


FIG. 1.—The Lattice Parameters of the Solutions of Vanadium in Gold.

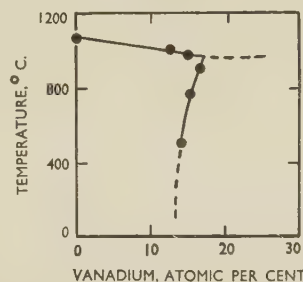


FIG. 2.—The Solubility of Vanadium in Gold.

limited by an electron concentration of about 1.20–1.40. If a "valency" of 3 is assumed for vanadium, the electron concentration at maximum solubility then becomes 1.35. This value of 3 is lower than the value of 4 or 5 suggested for metallic vanadium by Hume-Rothery, Irvine, and Williams.⁴ It does,

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† Technical Officer, Imperial Chemical Industries, Ltd., Billingham Division; formerly Research Metallurgist, Associ-

ated Electrical Industries Research Laboratory, Aldermaston, Berkshire.

however, support the division of the transition elements into two groups, as postulated by these authors on the basis of their chemical and physical properties.

It was also shown that the distortion caused to the gold lattice per atomic per cent. of transition element at maximum solubility was proportional to the difference in the atomic sizes. The distortion due to vanadium, which is 8.8% smaller than gold, is -0.0018 kX ;

this agrees well with the relationship previously determined.

ACKNOWLEDGEMENTS

The author would like to thank Miss J. O. Peters for assistance with the experimental work and Dr. T. E. Allibone, F.R.S., for permission to publish this paper.

REFERENCES

1. G. A. Geach and D. Summers-Smith, *J. Inst. Metals*, 1953-54, **82**, 471.
2. E. A. Owen and E. A. O'Donnell Roberts, *ibid.*, 1945, **71**, 213.
3. J. B. Nelson and D. P. Riley, *Proc. Phys. Soc.*, 1945, **57**, 160.
4. W. Hume-Rothery, H. M. Irvine, and R. J. P. Williams, *Proc. Roy. Soc.*, 1951, [A], **208**, 431.

A NOTE ON THE INFLUENCE OF GRAIN-BOUNDARY FLOW IN THE CREEP OF A LEAD-0.5% TIN ALLOY *

1588

By P. BROCK,† B.Met., Ph.D., MEMBER

(Communication from The British Non-Ferrous Metals Research Association.)

SYNOPSIS

The effect of grain-size on creep rate and the effect of stress and grain-size on grain-boundary sliding have been demonstrated on two similar specimens of a lead-0.5% tin alloy. One specimen, tested at a stress of 300 lb./in.², crept 51% in 32,000 hr., whereas another specimen, tested at 500 lb./in.², crept only 28% in the same time, as a result of recrystallization occurring during the test.

THE creep curves of a lead-0.5% tin alloy tested at constant stresses of 300 and 500 lb./in.² (Fig. 1) have demonstrated in a striking manner the effect of grain-size on creep rate and the effect of stress and grain-size on grain-boundary sliding.

The alloy was made from high-purity lead and tin and extruded at 100° C. The preparation, extrusion,

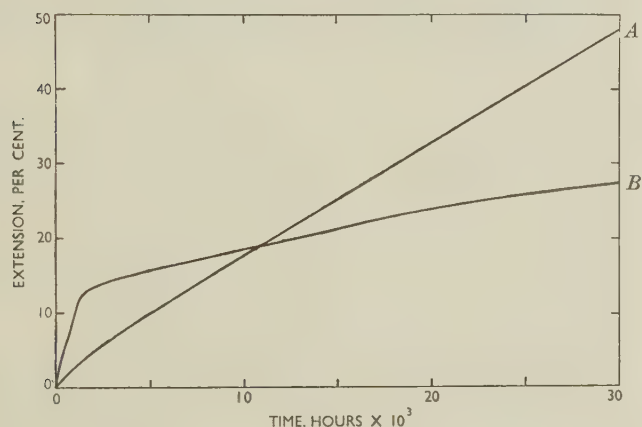


FIG. 1.—Creep Curves of a Lead-0.5% Tin Alloy under Constant Stresses of (A) 300 and (B) 500 lb./in.².

and testing procedure are described elsewhere.¹ After extrusion, the grain-size of the material was 0.008 mm.², and this grain-size did not change during storing for 32,000 hr. at 20° C. The structure at this stage is shown in Fig. 2 (Plate XXXI). It will be seen that a considerable portion of the grains contained twins.

The specimen tested at 300 lb./in.² crept 51% in 32,000 hr. The creep curve showed no inflection characteristic of recrystallization, but at this stage the grain-size had increased to 0.016 mm.² and most

of the grains were free from twins (Fig. 3, Plate XXXI). The creep curve of the specimen tested at 500 lb./in.², on the other hand, showed an inflection at 1000 hr. after an extension of 10%. The creep rate then decreased rapidly during the next 1000–2000 hr., so that at 32,000 hr. the extension was only 28%. The specimen then consisted of large grains of about 25 mm.² area, with numerous smaller grains and twins (Fig. 4, Plate XXXI).

McLean² has shown that the ratio of grain-boundary sliding to deformation within the grains during creep of aluminium increases with decreasing stress and grain-size. It appears that in the lead specimen tested at 300 lb./in.² grain-boundary sliding was the predominant process, so that the deformation within the grains was not sufficient to cause recrystallization; the small increase in grain-size which did take place was no doubt due to grain-boundary migration associated with the grain-boundary sliding.³ This view is supported by the twin-free nature of the grains, as a twinned structure would be expected if recrystallization had occurred.

ACKNOWLEDGEMENTS

The author wishes to thank the Director and Council of The British Non-Ferrous Metals Research Association for permission to publish this paper. The data used were obtained by L. M. T. Hopkin and C. J. Thwaites.¹

REFERENCES

1. L. M. T. Hopkin and C. J. Thwaites, *J. Inst. Metals*, 1953–54, **82**, 181.
2. D. McLean, *ibid.*, 1952–53, **81**, 293.
3. H. C. Chang and N. J. Grant, *Trans. Amer. Inst. Min. Met. Eng.*, 1952, **194**, 619.

* Manuscript received 9 August 1954.

† Investigator, British Non-Ferrous Metals Research Association, London.

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experiment or argument and, if possible, the essential parts of any new theory, treatment, apparatus, technique, &c.

It should contain the names of any new compound, mineral species, &c., and any new numerical data, such as physical constants; if this is not possible, it should draw attention to them. It is important to refer to new items and observations, even though some are incidental to the main purpose of the paper; such information may otherwise be hidden, though it is often very useful.

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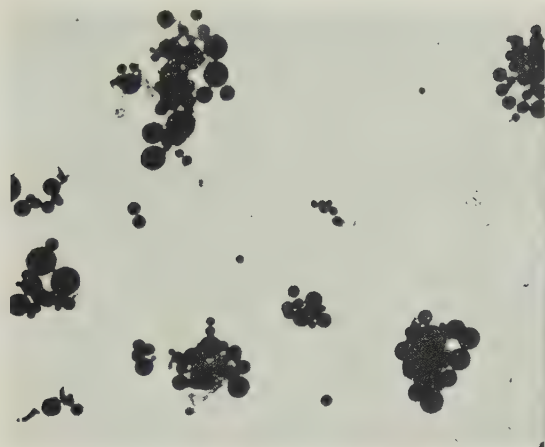


FIG. 16.—Electron Micrograph of Extracted Silica Particles Formed at 950° C. in Copper-0.3% Silicon Alloy. $\times 1500$.

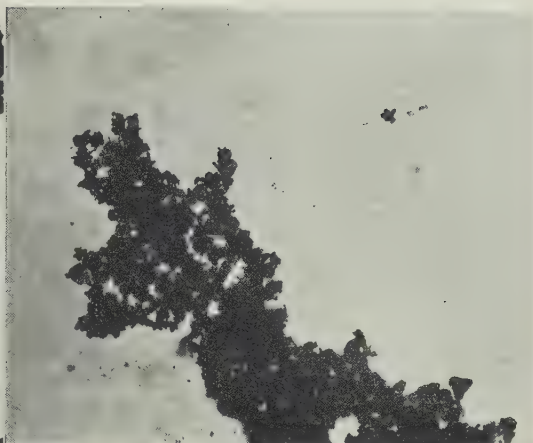


FIG. 17.—Electron Micrograph of Extracted Alumina Particles Formed at 900° C. in Copper-0.25% Aluminium Alloy. $\times 15,000$.

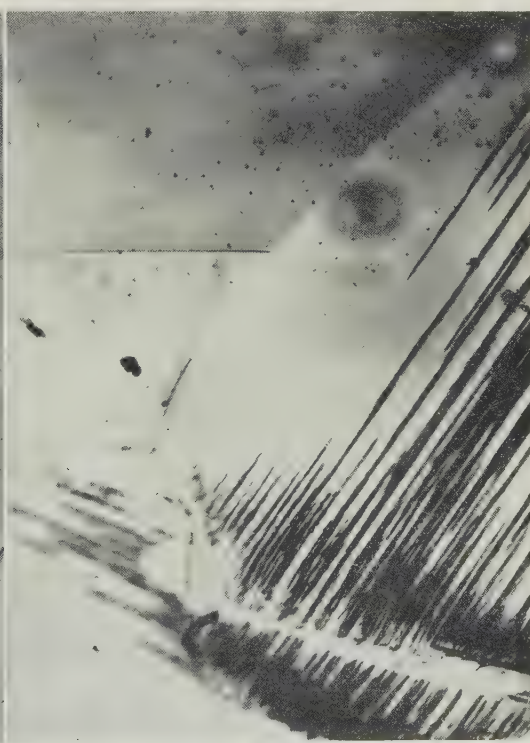
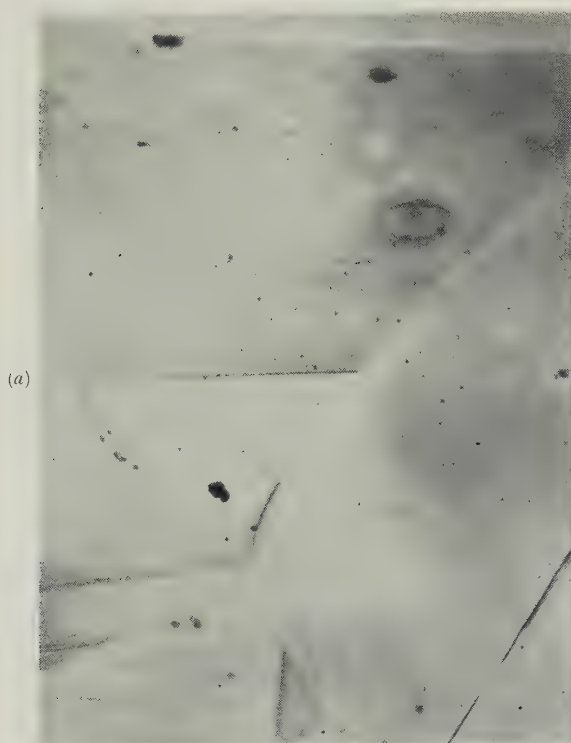


FIG. 18.—Copper-0.3% Silicon Alloy, Annealed at 900° C. Electropolished Chevenard fatigue specimen; half surface shear strain = 1.93×10^{-3} radians. (a) After 5000 cycles, (b) After 254,000 cycles. $\times 500$.

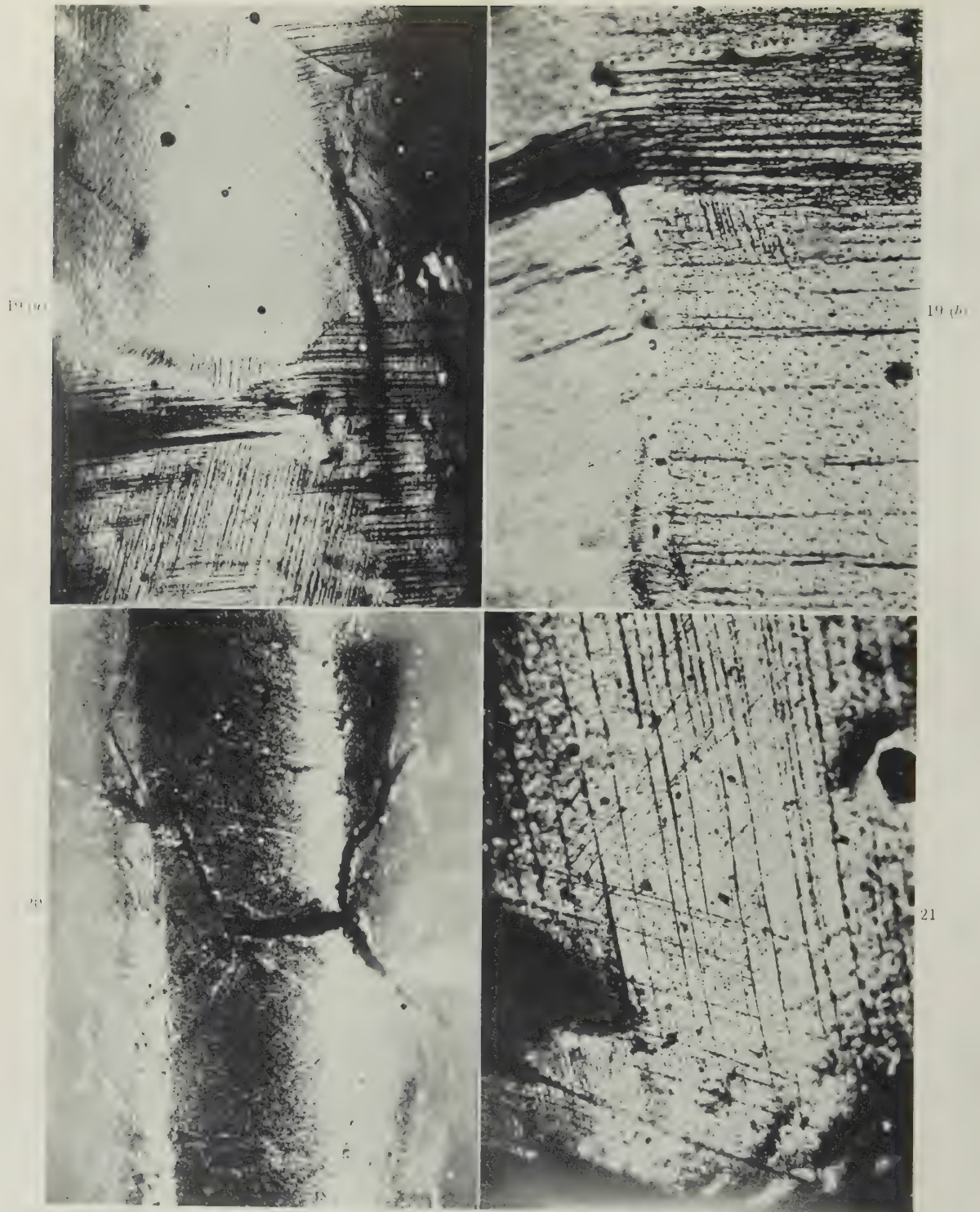


FIG. 19. Copper-0.3% Silicon Polycrystalline Specimen, Internally Oxidized at 900° C. Electropolished Chevenard fatigue specimen; half surface shear strain = 1.93×10^{-3} radians. After 200,000 cycles. (a) $\times 200$, (b) $\times 600$.
 FIG. 20.—Path of Fatigue Crack in Internally Oxidized Copper-0.3% Silicon Polycrystalline Specimen. Electropolished. $\times 70$.
 FIG. 21.—Copper-0.3% Silicon Single Crystal, Internally Oxidized at 950° C. Electropolished Chevenard fatigue specimen; half surface shear strain = 2.16×10^{-3} radians. Fractured specimen after 575,000 cycles. $\times 250$.

PHOTOMACROGRAPHS SHOWING RECRYSTALLIZED GRAIN-SIZE IN ALUMINIUM SINGLE CRYSTALS IN RELATION TO SURFACE NUCLEATION. $\times \frac{9}{10}$.

All specimens extended 20% and annealed (after etching) for 15 min. at 600° C.

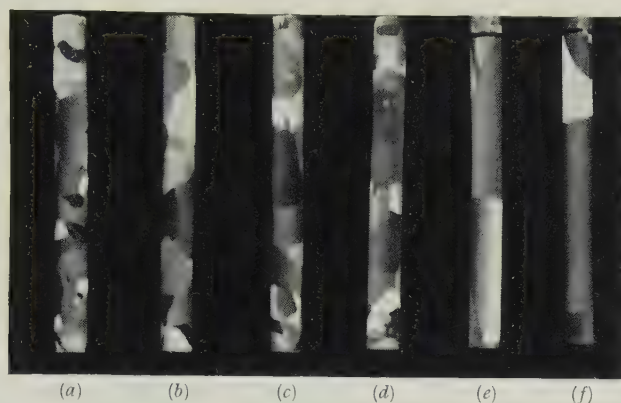


FIG. 2.—Crystal No. 5.

- (a) Not etched after extension.
 (b) Etched for 10 min. in 3% H_3PO_4 ; no metal removed.
 (c)–(f) Etched in hot 10% KOH ; 1.3, 2.5, 7.5, and 22.5×10^{-3} cm. of metal removed, respectively.

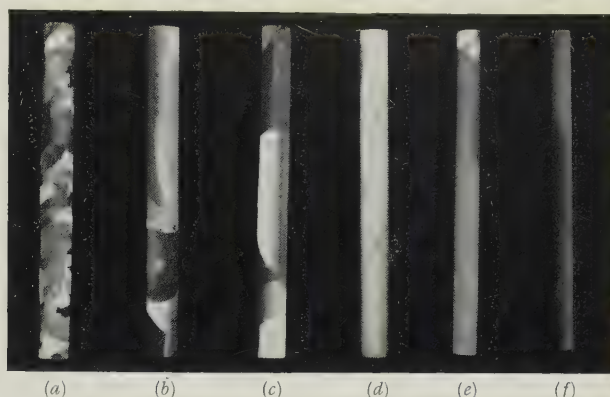


FIG. 3.—Crystal No. 4.

- (a) Not etched after extension.
 (b)–(f) Etched in boiling *aqua regia*; 1.3, 5, 10, 20, and 37.5×10^{-3} cm. of metal removed, respectively.

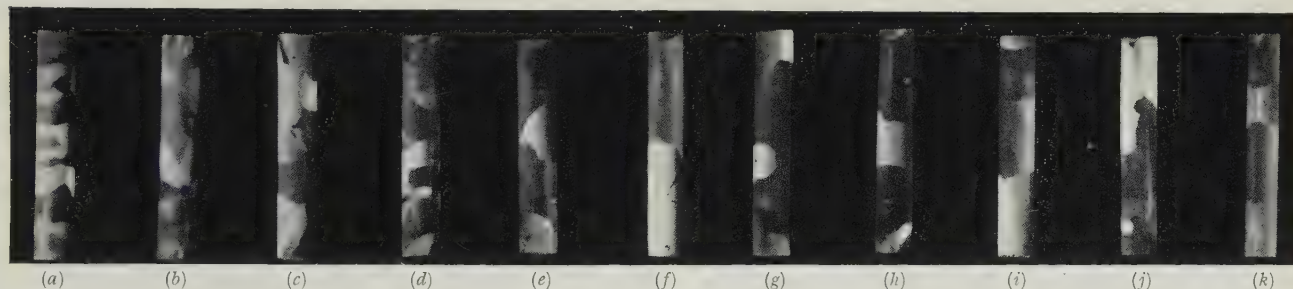


FIG. 4.—Crystal No. 11.

- (a) Not etched after extension.
 (b)–(k) Etched in Flick's reagent diluted to half-strength; 0.56, 1.7, 2.3, 3.2, 5.7, 9.1, 13, 24, 25 and 38×10^{-3} cm. of metal removed, respectively.



FIG. 5.—Crystal No. 15.

- (a) and (b) Etched for 20 min. in hot 10% NaOH ; extended under etch. (a) Not etched after extension. (b) Etched in NaOH ; 25×10^{-3} cm. of metal removed.
 (c) and (d) Etched for 20 min. in hot 10% NaOH ; washed, dried, held in air for 10 min., extended in air. (c) Not etched after extension. (d) Etched in NaOH ; 25×10^{-3} cm. of metal removed.



FIG. 6.—Crystal No. 14.

- (a) and (b) Immersed in Flick's reagent and pulled immediately. (a) Not etched after extension. (b) Etched in hot 10% NaOH ; 25×10^{-3} cm. of metal removed.
 (c) and (d) Immersed in Flick's reagent and pulled after 5 min. (c) Not etched after extension. (d) Etched in hot 10% NaOH ; 25×10^{-3} cm. of metal removed.

PHOTOMICROGRAPHS OF SUPER-PURITY ALUMINIUM DEFORMED BY FATIGUE.

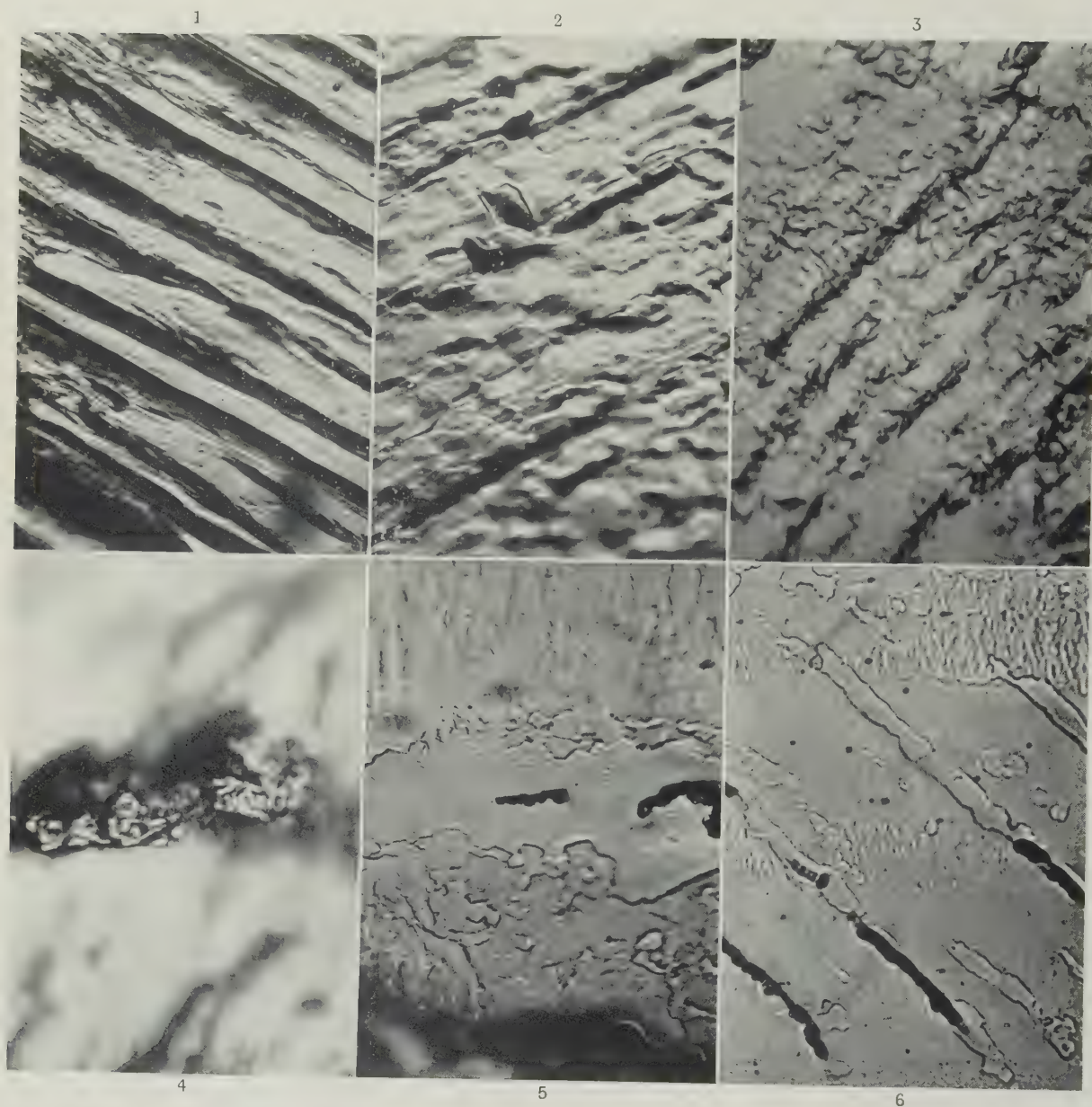
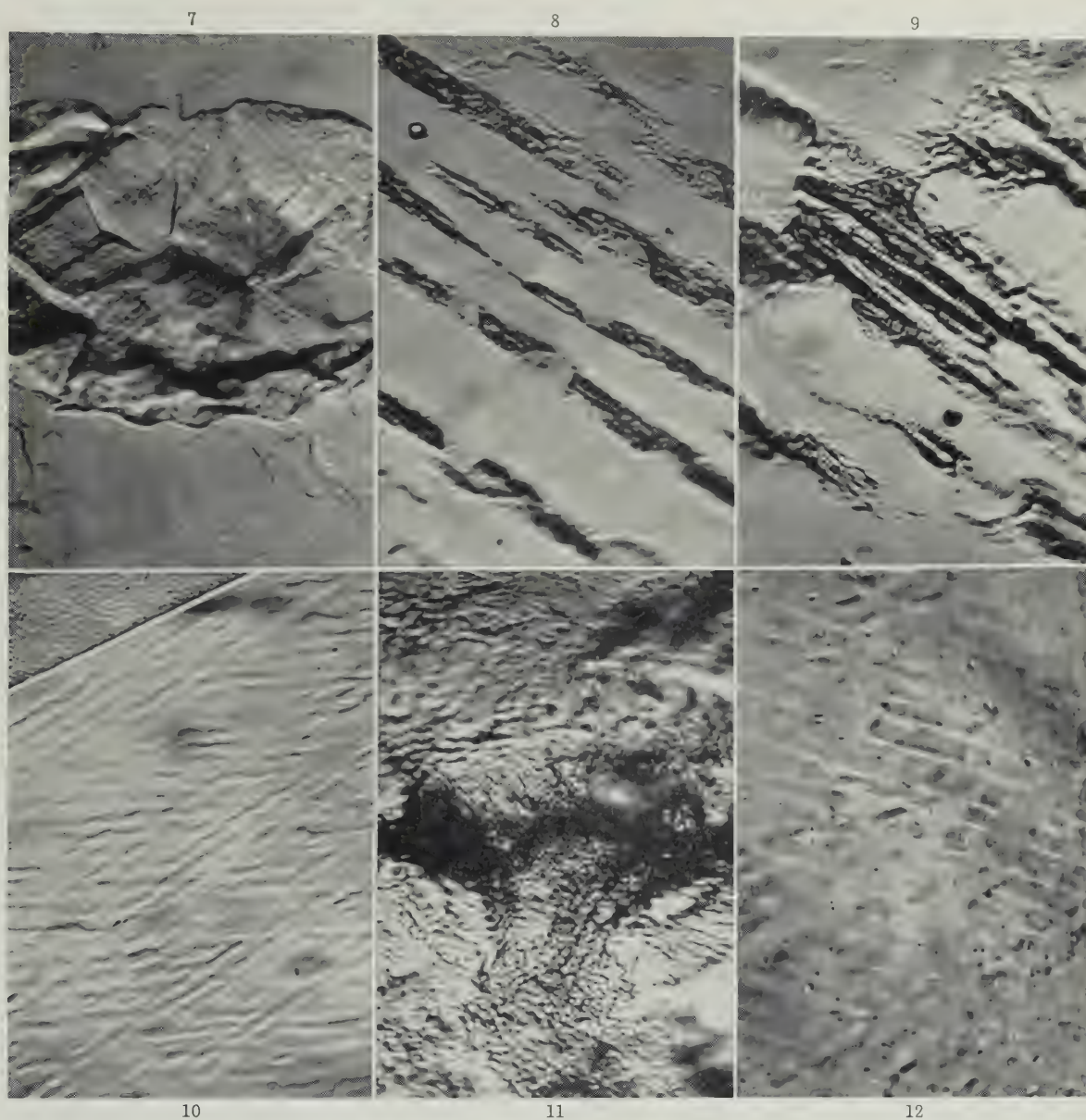


FIG. 1.—Slip Striations Produced by Cyclic Stresses. $\times 1000$.
 FIG. 2.—Sub-Boundaries Heavily Outlined by Slip Produced by Cyclic Stresses. $\times 1500$.
 FIG. 3.—Cold-Rolled Aluminium with Sub-Boundaries Outlined by Fatigue Stress. $\times 1500$.
 FIG. 4.—Surface Eruption Associated with Local Sub-Grain Growth. $\times 1500$.
 FIG. 5.—Sub-Grain Growth and Associated Cracks. $\times 1000$.
 FIG. 6.—Sub-Grain Growth Showing a Directional Effect. $\times 1000$.

PHOTOMICROGRAPHS OF SUPER-PURITY ALUMINIUM DEFORMED BY FATIGUE.

FIG. 7.—Fatigue Deformation in Enlarged Grain. $\times 1500$.FIG. 8.—Fatigue Deformation Produced at Liquid-Nitrogen Temperature. $\times 1500$.FIG. 9.—Fatigue Deformation Produced at Liquid-Nitrogen Temperature. $\times 1500$.FIG. 10.—Sub-Structure Produced by Fatigue at Liquid-Nitrogen Temperature (Etched). $\times 1500$.FIG. 11.—Surface Deformation Produced by Fatigue of Cold-Rolled Aluminium at Liquid-Nitrogen Temperature. $\times 1000$.FIG. 12.—Cold-Rolled Aluminium Fatigued at Liquid-Nitrogen Temperature, then Etched. (Phase Contrast.) $\times 1000$.

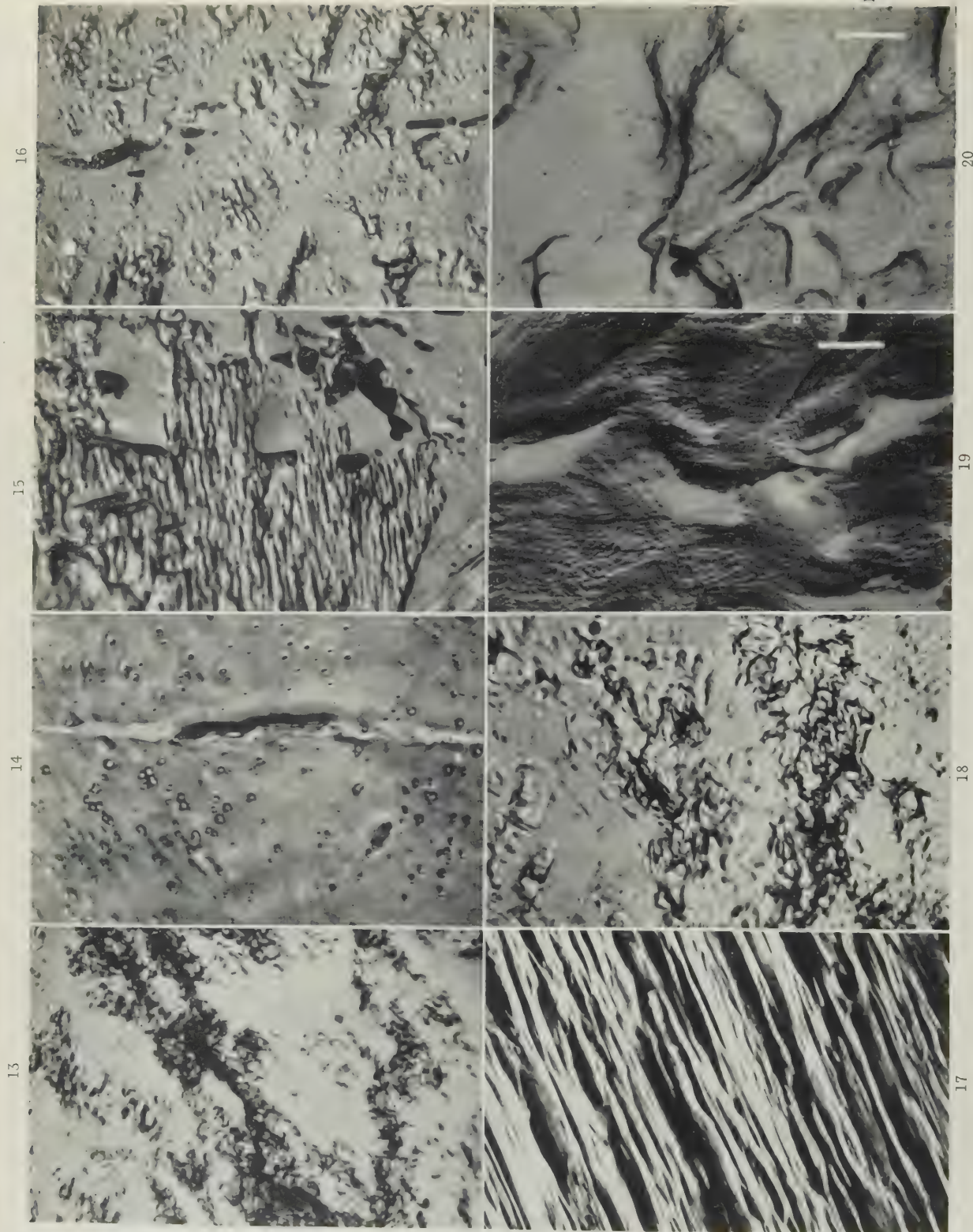


FIG. 13.—Fatigue Deformation of Al-1% Mn Alloy at Room Temperature. $\times 1500$.
FIG. 14.—Crack in Al-1% Mn Alloy Following Recrystallized Region (Phase Contrast). $\times 1200$.

FIG. 17.—Al-5% Zn Alloy Fatigued in Annealed Condition. $\times 1500$.
FIG. 18.—Al-5% Zn Alloy Fatigued in Cold-Rolled Condition. $\times 1500$.

FIG. 15.—Al-1.3% Fe Alloy Fatigued in Annealed Condition. $\times 1500$.
FIG. 16.—Al-1.3% Fe Alloy Fatigued in Cold-Rolled Condition. $\times 2000$.

FIG. 19.—Electron Micrograph of Cold-Rolled Pure Aluminium Showing Fatigue Deformation. $\times 11,000$.
FIG. 20.—Electron Micrograph of Cold-Rolled Pure Aluminium, Showing Fatigue Deformation. $\times 11,000$.

PHOTOMICROGRAPHS OF A LEAD-0.5% TIN ALLOY EXTRUDED AT 100° C.

Direction of Stress
↔FIG. 2.—After 32,000 Hr. Unstressed.
× 100.FIG. 3.—After 51% Creep in 32,000 Hr.
at a Stress of 300 lb./in.². × 100.FIG. 4.—After 28% Creep in 32,000 Hr.
at a Stress of 500 lb./in.². × 10.

ASSESSMENT OF QUALITY OF WROUGHT PRODUCTS * 1589

By W. G. SHILLING,† M.C., D.Sc., F.Inst.P.

SYNOPSIS

An outline is given of the system of inspection used by the Aeronautical Inspection Directorate (Ministry of Supply). Observations are made on various aspects of inspection, such as sampling and methods of test at various stages of production.

I.—INTRODUCTION

CONTROL of quality implies inspection, and the object of this introductory paper is to present the inspection viewpoint. Its scope is limited to various aspects of aeronautical inspection, so that, although the general principles should hold good, less than justice may have been done to other forms of inspection.

It may help those who are not familiar with its activities to give a brief outline of the way in which the Aeronautical Inspection Directorate functions. Most firms possess an inspection organization of their own. In the course of years this organization will have developed some very good methods of control and will have concentrated on the essentials. The Directorate tries to utilize this experience, to work with the firm, and to introduce only the minimum disturbance needed to ensure that the fundamental requirements are met. It does not nominate inspection staff, but one technically qualified member of the staff, who is not directly responsible for output, must be appointed to serve as a point of contact. He is called the firm's Chief Inspector, and through him all A.I.D. requirements and any necessary instructions are transmitted.

A firm is approved after steps have been taken to establish by detailed examination that the firm can inspect to the satisfaction of the Directorate. Thereafter the task of A.I.D. is to see that the approved standard is maintained. There are various ways of doing this. At larger units a resident staff may be appointed to maintain constant liaison, while other firms may be supervised on a visiting basis. With the limited A.I.D. staff, such visits cannot be lengthy enough to cover the whole of the work going on, so the visiting A.I.D. representative is encouraged on each occasion to investigate thoroughly one particular aspect of the process. This is considered better than taking a cursory look at the whole.

Any firm carrying out work for which the Director-

ate is the Inspecting Authority is called upon periodically—though not at any predetermined intervals—to supply material, so that checks can be performed in the A.I.D. laboratories of tests which have been done by the firm in the course of normal working. One of the easiest of these is chemical analysis, where the remainder of a sample already analysed by the firm may be collected and results compared. Other forms of testing are not so simple to check, especially where the sample is destroyed, as, for example, in tensile testing.

The checks must not be regarded as snoopers' traps; they are carried out solely to see whether the firm is operating within the agreed tolerances. The Directorate prefers any difficulty to be brought at once to its notice, so that all the help possible can be given towards removing it. Such is the basis of the A.I.D. inspection system. Its advantages are that it does not repeat work already well done, thus economizing in man-power; it does not delay despatch of finished products; it is readily adaptable to any degree of sub-contracting, and can be quickly expanded in emergency.

At the finished stage of wrought metal production much vital information is so hidden that it can be revealed, and then but partially, only by a very large number of destructive tests. Visual examination, which can include dimensional checking, and, if the nature of the article permits, a simple test such as a hardness test, are almost all that can be carried out. It is true that visual examination reveals surface defects and can sometimes provide a clue to other properties. Blistering on light alloys may, for example, indicate overheating, the orange-peel effect suggests unsatisfactory grain-size, and excessive scale on steel may point to decarburization. Even visual examination, however, requires certain preparation of the metal if the best results are to be obtained.

Visual examination seldom provides any indication

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of internal defects. With all materials, whether metals or non-metals, control must begin at the "melting pot" and cover all subsequent operations if it is to be effective. At one time a reasonably reliable verdict could be reached from a final test or final inspection. Nowadays a verdict based on such a test is totally inadequate, and it is essential for meticulous attention to be devoted to the successive stages of every process and treatment. In the attainment of modern efficiency, often expressed in the form of strength or power per unit of weight, two very important developments have occurred. The factor of safety is now such that decimal points matter, and the odd defect or the corresponding proportion of improper treatment cannot be tolerated. Side by side with this, more efficient materials have been evolved of which the designer naturally wishes to take the greatest possible advantage. There is still evidence, however, that the price to be paid if the designer is to secure the utmost value is not fully appreciated. Such materials must receive very careful treatment, and the conditions under which metallurgical operations are performed must be closely controlled.

As illustrations of the older and newer types of alloy the simple binary aluminium alloys may be compared with the more modern, so-called "high-strength" alloys. It has been suggested that the latter are "treacherous", but may not the correct descriptive word prove to be "fastidious"? So control, and with it, inspection, must be continually intensified to meet more and more stringent requirements. At times it is difficult for control and inspection procedures to keep pace with alloy developments, for the urge to utilize the better properties of a new product before all its idiosyncrasies are known, is very strong. The inspector cannot adopt too theoretical an attitude and forbid its use. Something must at times be risked if he is not to slow down progress and production too greatly. On the other hand, in the aeronautical world particularly, nothing unsafe must be allowed to pass, even if production and apparent progress do have to be sacrificed, for this might endanger morale and so hinder rather than encourage advances. The inspector must use his discretion and apply his knowledge of the technicalities involved, often with the exercise of a considerable amount of diplomacy.

If everything that has been suggested in the present series of symposia as good practice were always carried out, one might well ask whether inspection is really necessary. For there is nothing new in inspection; it is merely a means of ensuring that what should have been done has in fact been carried out. Even with the most enlightened practice, however, mistakes occur. These come within the scope of the well-known phrase "the human element", but there are also firms who aim near the outer ring of the target and so sometimes miss it altogether. Inspection is still essential therefore. But there is a much more fundamental reason than this, for with the best of intentions and with the exercise of the greatest care, it is still possible to deviate from the straight and narrow path. There is

no sudden change, no warning, and the only safeguard is reference to an outside, independent standard. The A.I.D. tries to provide such a standard throughout the industries with which it is concerned. The better the members of its staff can perform their duties, the less trouble there should be; nevertheless it is significant that when everything seems quiet we become uneasy!

In the following sections some aspects of inspection are briefly examined, particularly those which are sometimes overlooked and which are not dealt with elsewhere in this symposium.

II.—SPECIFICATIONS

The governing technical document of any contract is usually the specification. Specifications lay down requirements to be met by the product, and these vary greatly with the material or even with the same material for different end uses. Metallic materials usually have to comply with one or more mechanical tests, as well as with stipulations regarding composition, heat-treatment, dimensions, &c. Sometimes the specifications state the basis of testing or refer to other documents (e.g. British Standards L.100 and A.4). New specifications are often quite wide in their tolerances, for they must depend on experience to achieve the best within the specified limits. At times the experiences of different manufacturers lead them to adopt their own preferred tolerances, thus producing several slightly different ranges within the blanket cover of the specification. Events may develop in the reverse way, where the products of several manufacturers, differing but slightly, yet consistently, one from the other, may be covered by one specification. Thus, the limits of composition may appear to be rather wide, but the alternative of having a separate specification to suit each manufacturer's ideas is clearly undesirable.

The tests called for in the specification do not always yield results that are of direct use to the designer. It must be remembered, however, that the aim of a specification is to provide uniform material. The designer's requirements can be catered for elsewhere. They should, in fact, be established before large-scale production begins. Fatigue life under stipulated conditions is one such property. There are others, such as creep properties in alloys for use at high temperatures, which seem to need checking from batch to batch. A creep test is essentially time-consuming, so that, in the interests of production, compromise test conditions have to be arranged. There are, of course, other properties which cannot be specified, for they cannot be defined in measurable units. Microstructures, grain-size, dispersion of intermetallic compounds, are examples of these. The Directorate has drawn up Inspection Instructions in an attempt to cover some of these aspects, but it is surprising how often something arises which is new, and therefore not provided for. When this happens it is essential to take immediate steps to establish whether the point

involved is serious and demands recognition, or whether it can be disregarded. It may indicate a need to revise the specification, since difficulties in production may exist. It is the duty of inspection to clear up such problems, and this means liaison with the producer and with the design authority. Often a considerable amount of research may be necessary before the problem is solved, and to many inspectors this represents a very interesting side of their work.

Quite often the method of test is stipulated in specifications. The reason for this is that there may be several ways of performing the test, each of which may give slightly different results. Bearing in mind once more that the aim of a specification is to produce a reliably uniform material, the reason for selecting a test is obvious; or it may be that the specified method is known to be the most reliable. The inspector is continually looking for neater and quicker, though still trustworthy, methods of test and for more and more non-destructive tests; as well as for means of applying such tests at the point in production where they will, if they reveal serious defects, save most time and money. To refrain from testing until the product is finished is seldom good economics.

III.—TESTING

1. SAMPLING

The amount of testing, and how and when it is to be carried out, are factors of prime importance. The first essential is to decide from what amount of material a sample ought to be taken. The Directorate favours the batch system. A quantity made at the same time (i.e. during one shift of the same operatives), by the same methods, from the same raw material, is likely to be reasonably uniform and may be labelled a "batch", a representative sample from which may be expected to give a good indication of the quality of the whole. There may be limiting factors, such as the desirability of restricting the maximum size of a batch by numbers or by weight. Not only does the definition of a batch in this way render sampling more logical, but if the identity of the pieces of the material is maintained, any subsequently found to be defective can readily be traced and the quantity of defective material kept within reasonable bounds.

Good sampling should secure true representation, but since perfectly uniform batches are very rare, testing a single specimen from a batch may give most unreliable information if the results of that test are considered in isolation. Yet it is well-established practice to take a single specimen for tensile or impact testing from a batch. The saving factor is that normally a number of comparable specimens from similar batches are known to give test results which form a statistically uniform population of values. A series of such results, plotted on some form of quality-control chart, provides a picture of how successful control has been. Thus, the statement that a batch may be condemned on the results of a single test is only par-

tially true. A batch may be accepted on the basis of such test, but if the test results do not come up to specification it is usual to treble the sample size and so obtain much more information about the batch in question.

It is, of course, essential that methods of test should give reproducible results, because the variations inherent in the test methods must be included in the specification tolerances.

2. COMPOSITION AND ANALYSIS

There is a school of thought which tends to minimize the importance of composition and places reliance rather on performance. One stated objection to a specified composition has been that it discourages research and development. Most metallurgists prefer to know composition before starting on any serious investigation, however, and it is unlikely that there are many manufacturers who would not come forward with a new product if they knew it to be better than the old. The A.I.D. normally regards an accurate knowledge of composition as an essential starting point, for much can often be foretold or expected from such information.

Composition is usually determined on a sample selected during casting, due attention being paid to possible segregation, which in turn means attention to methods of melting, casting, and sampling. Segregation is difficult to define, and the limits difficult to fix, but the state of knowledge and practice nowadays generally yields products within practical tolerances. A batch for analysis may consist of one furnace melt or one crucible melt or the products of a number of crucibles (or furnaces) which are to be mixed before casting. In continuous casting, it is possible to choose a unit quantity, such as a proportion of a charge poured at one time, but true batch sampling is obviously difficult. It is better to deal with the problem in the reverse way and so arrange batches that the resulting products can be grouped and traced back, if the need arise, to a reasonably restricted quantity of material. Methods of analysis must, of course, be accurate and reproducible to well within the tolerances permitted by the specification.

3. NON-DESTRUCTIVE TESTING

Radiology is the best established of non-destructive methods. It is extremely valuable for castings, but not so useful for wrought products, because many of the defects tend to become attenuated or get welded up on extrusion or forging.

Many defects can, however, be revealed by ultrasonic methods, e.g. voids, porosity, or discontinuities in thick pieces of metal (steel rods, blades, light-alloy forgings, extrusions), large segregations of metallic compounds, and occluded foreign matter. The application of the method is limited to fairly thick sections and to comparatively simple shapes. As all these defects are much more evident in the as-cast condition, it is obvious that the cheapest and easiest way to find them is by ultrasonic exploration at the billet stage.

For steels, magnetic flaw detection is invaluable in detecting defects which break surface. Care is necessary to magnetize correctly (current method or magnetic-flow method), since defects are best revealed when they lie at right angles to the flux lines. Unless the operator is very experienced, the method should be used as an aid to inspection rather than as a means of assessment, and the ill-effects of under- or over-magnetization must be borne in mind.

For non-ferrous materials, other methods are available, some form of indicating penetrant being generally used. Chromic-acid anodizing, followed by a light wash in water and a reasonable waiting period, is highly effective in revealing defects in light alloys. The familiar oil-and-chalk method, of which there are many modern variants, including the use of fluorescent pigments, is very useful. All these, of course, are operative only if a defect breaks surface.

Defects revealed by non-destructive test methods fall into two categories: (1) those likely to be associated with a batch of material, such as excessive inclusions, and (2) those affecting isolated pieces (e.g. laps in bars or forgings).

4. TENSILE TESTS

The basic properties of strength and ductility are measured by tensile testing. In addition to tensile strength, elongation, &c., aeronautical specifications usually call for 0.1% proof stress determinations. Incidentally, the determination of the proof stress of aluminium-clad aluminium alloys presents some difficulties, for they give two lines of proportionality in the stress/strain diagram, and a decision is needed as to which line to take. On theoretical grounds, the first should be used, but a good case could be made for choosing the second. However, recent work of high accuracy seems to throw the entire question again into the melting pot, for it indicates that there may be a whole series of "lines of proportionality".

Usually one test per cast or heat-treatment batch is carried out, and if the results fall below specification, two further tests are made. These do not adequately ensure uniformity of the batch, because some 25% defective specimens would be necessary to give an even chance of finding one in the above-mentioned three samples. For this reason some additional 100% check is advisable, and this often takes the form of hardness or proof-bend tests. Instead of a full tensile test, which is destructive, proof-bend determinations are sometimes employed, especially for tubes, to achieve the ideal of 100% testing. Bending is limited to the elastic range, and the test demonstrates only that the proof-stress value is in fact within specification requirements.

While on the subject of tensile testing, a general plea may perhaps be made for greater attention to be paid to maintaining the accuracy of the machines used. They often need more than an annual check by the makers or by some other recognized authority. Finally, a satisfactory tensile result does not, *per se*, indicate that all is well.

5. OTHER TESTS

Other tests not so regularly used have specific uses. Among them are:

(a) *Impact Tests*.—These provide an indication of satisfactory heat-treatment conditions, as in steel, where unsatisfactory hardening or tempering temperatures may result in low values. They can also give indications of unsuitable forging techniques or temperatures.

(b) *Bend Tests*.—These are often used to give an indication of the ductility of sheet and strip metal which is too thin for such information to be obtainable from tensile test pieces. The method of performing this test by pressing the specimen into a lead block by means of a former is not sufficiently discriminating. The free-cone bend test is preferable.

(c) *Etching Test*.—This is applied to light-alloy extrusions to indicate whether they are free from extrusion defects. The specimens are usually taken from the back end of each extrusion length.

IV.—USE OF STATISTICS

Much useful information may be obtained from the correlation of test results by elementary statistical treatment—the plotting of histograms and the drawing of the corresponding Gaussian envelope. Ignoring for the moment the fact that such curves contain also the experimental errors inherent in the methods of test, the two quantities of interest, particularly to the inspector, are the difference between any value and the mean (X and \bar{X}), commonly called the deviation, and the root mean square of the deviations of all values (σ), commonly called the "standard deviation". In addition to providing him with an assessment of the standard of production, these enable the inspector to decide what testing inaccuracies and what methods of test he can permit, for it is of economic importance not to demand an unnecessarily high degree of accuracy.

Further, a skewed histogram indicates the existence of some abnormality. Among the explanations for such abnormalities, the following may be quoted as examples:

(1) Inclusion of unequal numbers of cut-up test-pieces taken from different locations in castings.

(2) Inclusion of results from specimens which had undergone unequal amounts of cold working.

(3) Tensile testing at different states of ageing of heat-treatable light alloys.

(4) Mixing of tensile results obtained from different thicknesses of sheet materials.

Other histograms may give a reasonable distribution, but show a tendency to displacement of the norm. Such displacements may be due to causes of which the following are examples:

(i) In measuring hardness-test indentations some operators tend to read high and others low.

(ii) In general, results obtained by titrimetric analysis tend to be high.

(iii) In general, results obtained by gravimetric analysis show a tendency to be low.

A histogram which cuts off sharply at the specification minimum obviously calls for an explanation.

In some cases a distribution of no discernible form may be obtained. This may indicate an unsuitable method of test. For some time such results were found for the elongation of cast test-bars, and the explanation proved to be that, with materials of such low ductility, the extension was not being correctly assessed by using normal methods. The introduction of a satisfactory method of measurement resulted in a normal distribution being obtained.

Such elementary statistical treatment is being increasingly applied to inspection methods, but the approach must be made warily. For dealing with large quantities of small parts (e.g. heat-treated bolts and nuts and zip-fastener parts), and for the assessment of spot welds, the method has been very satisfactory and has taught us much about sampling. Analyses of results for tensile strength and ductility, and analyses of the variation of check tests between various authorities, are also interesting subjects for treatment. But where only one or two parts per machine are being produced and failure would be catastrophic, application of the method is not regarded as suitable.

V.—HEAT-TREATMENT

The symposium includes papers dealing with the heat-treatment of particular metals and alloys, so that only some points of purely inspection interest will be mentioned here. The two main purposes of heat-treatment are:

(1) To bring a material into a condition suitable for manipulation; this is usually some softening or annealing process.

(2) To obtain the optimum values for the required properties, often involving a balance between strength and ductility. The best properties of heat-treatable light alloys are obtained only by solution-treatment, quenching, and ageing (natural or artificial).

1. PROCESSES FOR ALUMINIUM ALLOYS

Three distinct processes may be included in the heat-treatment of aluminium alloys: annealing, solution-treatment, and ageing; in each case a uniform and carefully controlled procedure is essential. It is indeed in heat-treatment that the "fastidiousness" of the high-strength alloys, mentioned earlier, manifests itself most clearly. A.I.D. Inspection Instructions on the subject may, to those familiar with heat-treatment, seem dull reading and at times appear to state the obvious. It is remarkable, however, how often the obvious is not being observed. Earlier Inspection Instructions would sometimes omit simple and well-known requirements. We have learned now to put them in.

Those who manipulate high-strength alloys should not forget that the ageing curve rises very steeply at

first. With some alloys all work should be completed within 2 hr. of quenching after solution-treatment, if the best and most reliable results are to be obtained. For most important applications the efficiency of heat-treatment is assessed by some test for mechanical properties, but such tests alone are not really adequate. They should be backed by evidence of satisfactory processing, including such aspects as pyrometry, furnace charging, manipulation, and cooling.

There are four conditions in which heat-treatable material may be found:

A. Annealed.

N. Solution-treated and requiring no precipitation-treatment.

W. Solution-treated and requiring subsequent precipitation-treatment.

WP. Solution- and precipitation-treated.

It becomes essential, therefore, to avoid "mixes" and to verify the actual condition at all manufacturing stages. A.I.D. requires all material to be marked as indicated in the list above, with letters in an ink which will disappear at the next operation. A useful test, but one that is of use only to check uniformity when all operations have been correctly performed, is that of hardness. With steel a reasonable correlation exists between tensile strength and hardness, but with light alloys the relationship is not so satisfactory and, because heat-treatment is used to raise the tensile strength of light alloys and is critical, it is necessary to establish tolerances experimentally if hardness testing is used as a method of assessing strength. The minimum permissible is linked, in terms of percentage difference, to the value given by the test sample, the tensile strength of which has been determined. Obviously the nearer the test-sample results are to the specification minimum, the less is the difference that can be permitted. This is covered by the X% clause.

2. FORGINGS

Extrusion and the rolling of bar are processes fundamentally similar to forging, since all these methods squeeze the (usually heated) material into the required shape by pressure. However, whereas there is some constancy in shape, cross-section, and grain flow in bars or extrusions, a forging may exhibit great variations from place to place in both cross-section and shape. The longitudinal and transverse properties of extrusions and bars differ, and this difference becomes much more pronounced in forgings unless proper precautions are taken. In a bar the grain flow is more or less in one direction, and in most cases the bar can be used in such a way as to take advantage of this grain flow, although for larger cross-sections the test procedure begins to resemble that required for forgings. In a forging it is often difficult, if not impossible, to ensure that the grain flow in all parts lies in the optimum direction. The difficulties are intensified by the modern design tendency to make complicated shapes all in one piece, instead of employing the older method of building them up from separate

sections. Therefore, quite a lot of experimentation and testing must be carried out to establish that the forging technique is sound. After this has been done, the aspects to be considered are much the same as for other metallurgical operations. The selection of the right material, taking care that correct temperature and times are employed everywhere, the cooling arrangements, and the heat-treatment conditions have all to be covered.

In general, too high a temperature means overheating, with a consequent serious deterioration in properties, rendering the forging fit only for scrap. Too low a temperature usually leads to excessive work-hardening, causing cracks and ruptures.

Sampling for test purposes is more difficult in forgings than in forms having a regular cross-section. There are two main types of procedure:

(i) Samples of the material, integral with or separate from the forgings, are heat-treated with the forgings. As the material has usually been proved at some earlier stage, these samples serve mainly to verify the correctness of the heat-treatment.

(ii) Samples are cut from one or more forgings in each batch. In addition to providing a check on heat-treatment, these can provide information about the forgings themselves.

The first method needs to be supplemented by previous experience and/or by proof loading or actual running tests on the finished part made from the forging. For some highly stressed structural parts of aircraft, an elaboration of the second procedure is described in British Standard L.100. Test-pieces are cut from agreed locations at the beginning of production, after any significant change has been made in the pattern, forging stock, or forging technique, and at certain intervals during production. In addition, heat-treatment conditions are controlled by procedure (i) above.

Recent manufacturing procedures tend to use plates of the order of 3 in. thick and to machine large parts from them. In these the directional properties are very pronounced. As an example, the following results were obtained from a plate of high-strength alloy (D.T.D.363):

Direction	0.1% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Elongation, %
Longitudinal . . .	30	34	7
Transverse . . .	30	33	4½
Perpendicular . . .	28½	29	2½

Porosity often constitutes a danger in such plates, but as they are usually machined with deep recesses to form a thin plate with stiffeners, assessment of porosity is not difficult.

VI.—FINISHING PROCESSES AND SURFACE TREATMENTS

Surface-finishing processes are too numerous and varied for it to be possible to do much more than list them. No apology is made for including them, however, for almost all otherwise completed and satisfac-

tory wrought products can be spoiled by incorrect finishing procedures. The damage is not merely confined to the appearance; the physical properties can also be seriously impaired.

The following list is representative of finishing treatments: Preparation of metals for protection against corrosion, cleaning before plating, anodic oxidation, pickling of steel, nitriding of steel, soldering and brazing, welding, phosphate process, building-up by nickel or chromium plating, and electroplating.

Years of practical use and experience have established the conditions necessary for successful operation. Most of these are critical, and the secret of success lies in paying careful attention to a surprising amount of detail.

There are usually three stages in such work:

(1) *Preparation of the Surface*.—Utmost cleanliness is the primary requirement, but certain technical precautions are necessary. For example, cathodic pickling of high-tensile steels for aircraft use is not permitted (except for alkaline cathodic degreasing in certain cases) for fear of causing hydrogen embrittlement. For the same reason acid pickling is not allowed for this material for aircraft use.

(2) *Processing*.—A strict control of detail is essential, including composition of the electrolyte, procedure for mounting and introducing components into the bath, size and type of anodes, current, temperature, time, method of washing and drying. Shape and position of the electrode and throwing power of the electrolyte all affect the thickness and evenness of the coating, &c.

(3) *Inspection of the Product*.—Visual inspection of the finished part can provide a great deal of information. A suitable batch for inspection purposes is usually a vat or barrel load, and it is desirable to test each batch. Porosity may be assessed in several ways. For example, cadmium-plated steel parts can be tested by immersion in 1% hydrochloric acid, pinholes being revealed by hydrogen bubbles. Tin coatings may be immersed for some hours in hot distilled water; any rust spots that appear indicate pores. Thickness, both local and average, should be measured. A good test for adhesion is still needed. Applications of processes in the aeronautical field vary from mass treatment of small screws to individual treatment of an undercarriage of the order of 12 ft. in length, so that no universal method will apply and each job has to be treated on its merits.

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THE CONTROL OF QUALITY IN HEAT-TREATMENT 1590 AND FINAL OPERATIONS IN THE PRODUCTION OF ROLLED, EXTRUDED, AND DRAWN ALUMINIUM AND ALUMINIUM ALLOYS *

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SYNOPSIS

Aspects of heat-treatment and final fabricating practice that should be controlled to ensure a satisfactory quality in the production of rolled, extruded, and drawn aluminium and aluminium alloys are discussed. The operations covered include sheet shearing from coil, flattening, finish shearing, slitting, blanking, straightening of sections, drawing and finishing of tubes, inspection and packing. Some practical aspects of heat-treatment are also dealt with.

I.—INTRODUCTION

IN the heat-treatment and final operations involved in the production of wrought aluminium and its alloys, it is necessary to exercise a control of quality and operating conditions at least as close as that required in the earlier processes of melting, casting, hot and cold rolling, extrusion, &c. If defective material is produced during the concluding processes of heat-treatment, &c., not only is the cost of these processes wasted, but so also is the usually heavier expense of the earlier processes.

The qualities which need control during heat-treatment and final operations are as follows :

- (a) Dimensions.
- (b) Shape, i.e. flatness and straightness of rolled sheet and strip products, and the straightness and accuracy of profile of extruded and drawn shapes.
- (c) Mechanical and physical properties, for example, tensile properties, elongation, grain-size, &c.
- (d) Surface and edge quality in respect, for example, of colour, stains, texture, and freedom from blemishes, such as scratches, abrasions, holes, kinks, &c.

Many of these qualities are affected by the earlier processes referred to above, and the controls which are exercised at those stages to ensure optimum quality have been very adequately described in previous papers by King and Turner¹ and by Smith and Swindells.² If the quality of the product has

not been properly controlled in the early stages, it is often impossible to rectify the damage in the heat-treatment and final operations. For example, in the latter processes it is not possible to correct gauge variation which has occurred during rolling; nor, in general, can faulty properties resulting from incorrect temper-rolling conditions be subsequently rectified. However, there are some departures from the desired quality caused by inadequate control in the earlier processes, which can be put right in the later ones; for example, an imperfect as-rolled shape may be corrected to some extent in the final operations. Further, a well-controlled system of process-scrap collection and segregation at all stages of the final operations is of considerable assistance to the remelting department in ensuring that metal of the correct composition is cast. It should also be remembered that inspection of the finished product is one of the final operations, and it is during inspection that the final control of quality is exercised.

The present paper describes, under each main product group, the various processes employed and the precautions, in respect of both process conditions and plant used, which should be taken to ensure that material of the required quality is produced. The main product groups have been defined as follows :

- Flat sheet, plate and circles, non-heat-treated.
- Coiled strip, non-heat-treated.
- Heat-treated sheet and plate.

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Heat-treated coiled strip.

Extruded and drawn shapes :

- (i) Non-heat-treated extrusions.
- (ii) Non-heat-treated extruded and drawn products.
- (iii) Heat-treated extruded, and extruded and drawn products.

Of course, some final operations are common to two or more product groups; for example, sheet shearing is common to both non-heat-treated and heat-treated material, and in such cases the control of quality in the particular operation will be dealt with under only one of the products concerned.

II.—FINAL OPERATIONS FOR NON-HEAT-TREATED FLAT SHEET AND PLATE

These materials form the greatest bulk of light-metal products, and are used in various purities and alloy qualities. Commercial 99% pure aluminium forms the largest proportion; the aluminium-1½% manganese alloy, which has some 25% greater strength than the 99% pure metal, forms the next largest category; while aluminium-magnesium alloys with 2½, 3½, 4, or 5% magnesium, usually containing also small quantities of manganese or chromium, are used in smaller amounts.

Flat sheet may have been produced by rolling on hand or throw-over mills, or from coiled strip, which is now rolled up to 6 ft. wide. The latter is the more widely used and economical method of producing sheet in large tonnages. There is not a great deal of difference in the final processes required to flatten, cut to size, and anneal (if necessary) the two types of sheet. The strip-rolled product usually runs more true to, and more uniform in, gauge from sheet to sheet and across the width.

Plate is generally produced flat on hot mills in gauges down to ¼ in., in the 3½, 4, or 5% magnesium alloys.

1. CONVERSION OF COILED STRIP TO SHEET LENGTHS

To cut coiled strip into sheet lengths, repetitive shearing is necessary, and this is usually automatic. In all machines for this purpose, there is an arrangement for paying out the strip from the coil from a roller coil-box or from between cones. The strip is then passed through a roller-leveller to take out the curvature and flatten the strip; then sheared and lastly delivered to an over-running belt conveyor from the end of which the lengths of sheet are piled on a stillage or platform truck. In some simpler types of machine, the shear is a fixed guillotine, and the leveller works intermittently, in the simplest form with hand control, and in more advanced forms with automatic mechanical or electric control. The strip runs continuously in the most advanced machines, and these have a flying shear, either of a moving-head guillotine type (non-raked to ensure squareness of

cut), or of a revolving-drum type, the former being the more usual. In either case, the linear motion of the flying shear over the distance required to make the cut must be as nearly uniform as possible, and accurately matched to the constant velocity of the strip; otherwise shock marks across the sheet may be formed at the point where the strip is leaving the leveller at the instant of cut, especially if the shear is over-running.

The gearing of these machines is complex and must be capable of adjustment to cut any required length between the minimum and maximum given by the machine. The coil pay-out arrangement must be such that the motion of the strip is absolutely uniform, and there must be no occasional or periodic variations of back-drag, as this might give rise to slight slip in the leveller rollers, causing variation of sheet length. Where roller coil-boxes are used for the pay-out, the rollers should be driven at a controllable speed, so that a slack loop is maintained in the strip fed to the roller leveller. For accurate squareness of cut, the coil must be guided, which is best done by vertical bottom-guide rollers in the coil-box. The rollers of coil-boxes must be of fine surface free from blemish, or resiliently covered with felt or rubber, as any particles adhering to hard rollers would tend to mark the unwinding strip, owing to the superincumbent weight of the coil. It is necessary for coils to be placed in the coil-box without slack developing between the turns; otherwise there may be interlap movement during uncoiling, which is likely to cause adjacent surfaces to scratch each other. Cones cannot be driven without risk of loosening the coil, but it is usually sufficient that the leveller pulls the strip off the lightly braked cone-mounted coil. With the fixed-shear, automatic, intermittent-feed type of machine, driving of the coil is essential, allowing a loop to form before the leveller.

With the flying-shear type of machine, running at uniform speed, it is possible to incorporate a side-trimming machine with driven circular cutter knives, which can trim ½–1 in. off each edge and leave a strip true to width and with clean edges, the scrap being led from the knives down chutes for disposal. The edge-trimmer is located between the coil and the leveller, and there is a pair of driven pinch-rolls between the trimmer and leveller to assist in holding a slack loop before the leveller for the sake of uniformity of the sheet length.

Piling of the sheets can be done by delivering direct from the outgoing belt conveyor on to the pile with a stop at the end, and for this it is an advantage if the leading edge of the sheet has an upward, not a downward, burr; or the pile may be formed on an automatically descending platform, a light upward air-jet helping to float the sheets along. With large sheets, it is preferable, in order to avoid scratches, to carry the sheets along a narrow pull-off bar (which may be roller-topped along one edge), from which the sheets are pulled sideways by hand and laid flush on the pile against a back plate.

In theory, a slitting flying shear should be able to deliver flat sheets cut dead to size. While it is possible to obtain dimensions within commercial tolerances, it is not usual for the highest standard of flatness to be attained in the sheets as sheared from the coil. This is because the strip in the coil from the rolling mill is usually not dead flat, owing to slight differences in fibre strains from the mill, although no gauge differences are perceptible. The non-backed-up type of roller-levellers fitted to flying shears are usually not capable of imparting much greater flatness than is involved in taking out the coil curve, but it appears necessary to use this simple type of leveller to obtain the high working speeds that are required, namely 150–400 ft./min., with maintenance of high surface quality in the sheets.

To maintain the leveller rollers free from adhering solid particles, which would imprint indents on the passing strip, or undue oil film, which would mar the appearance and might impair length-accuracy, continuous wiping of the rollers by felt-backed, cloth-faced wiper boards, above the top rollers and below the bottom ones, is advisable.

A length accurate to $\pm \frac{1}{8}$ in. can be maintained on wide flying shears, and to $\pm \frac{1}{16}$ in. on the lighter machines and on hand-controlled intermittent shear machines. The accuracy from automatic intermittent machines is not quite so good.

2. FLATTENING OF SHEETS

The degree of flatness demanded in sheets for many purposes, such as cabinet sides, motor bodies, and panels of various kinds, is very high. A somewhat lower standard of flatness is, however, satisfactory for many commercial purposes. The flatness is usually assessed by visual inspection, the sheet, laid horizontally on a flat surface, being viewed from a very oblique angle. Seen thus, the imperfections, if any, are much more apparent than if viewed at right angles to the surface. The most common imperfections are: general longitudinal curvature; transverse curvature; longitudinal waviness, which may be due to central slackness (underpinched in rolling); lateral slackness (overpinched in rolling); intermediate quarter-band slackness; rolling ripple, i.e. transverse slight bends which may vary from about $\frac{1}{4}$ to 1 in. pitch or even longer; "drum marks" or coil-bore collapse marks, which are longer-pitched and more pronounced; and shock marks from imperfectly adjusted flying shears.

These imperfections all originate in the rolling or in immediately following processes, and it is the function of flattening to make the sheets as flat and ripple-free as possible. There is a limit, however, to the extent to which imperfections can be removed, and it is, therefore, of the utmost importance that rolling and strip-shearing practice should produce ripple-free sheets of satisfactory as-rolled flatness.

The sheet-flattening operations are roller-levelling and stretching (or stretcher-levelling), the latter usually being carried out in hydraulic machines.

For sheets required to be of good commercial flat-

ness, stretcher-levelling alone is usually sufficient if the sheets come from the mill in a reasonably flat state. When the highest degree of flatness is desired, it is often necessary to give the sheets a roller-levelling operation before stretching; this increases cost.

3. ROLLER-LEVELLING

The simple two-high roller-levellers, as used for rough flattening on flying shears, are not adequate for finish flattening, owing to the large diameter of their rollers. The roller-levelling process consists of alternately bending the sheets as they pass through the rollers, and it is necessary to exceed the elastic limit of the outer fibres of the sheet in order that some plastic deformation can take place. From bending theory, it is clear that smaller-diameter rollers give a higher stress for a given sheet thickness in a given material, and that for a given stress, the diameter of the rollers must be smaller, the thinner the sheet. This leads to the use of small-diameter rollers for precision levellers, and as these must be of full width and are therefore flexible, they are prevented from deflecting by rigidly supported backing-up rollers located across their length. The work rollers are driven, and the back-up rollers run idle in contact with them, being carried by stiff transverse beams.

The adjustments of these machines necessary to impart the necessary flattening include:

(a) General penetration of the work rolls to ensure that the passing sheet is forced sufficiently to take the bend of the work rollers. Excessive penetration is not used and might cause the front edge of the sheet to run into the back-up rollers.

(b) Rocking penetration (fore and aft). The rocking arrangement permits the work-roll penetrations to be considerable at the ingoing end and lighter at the outgoing end, thus ensuring that the sheet comes out flat without curve.

(c) Differential lateral penetration. The back-up rollers are arranged in 3 or 5 rows laterally, and it is usual to arrange for each row to be capable of bending the work rolls below themselves only, by separate adjustment. This gives local increase in penetration and does have some moderate effect in taking out lateral variations in flatness, but the diameter of the work rollers, which is the most potent factor, cannot, of course, be changed. For most purposes, it is satisfactory to use uniform lateral penetration, and to keep the support rollers uniformly in contact with the straight-work rollers, one advantage of which is that the work-roll surfaces will wear longer without deterioration by marking from certain rows of support rollers.

The drives to the work rolls must run true, as otherwise irregularities in rotation will show up as ripples on a sheet. For the same reason, all rollers must be ground truly straight, cylindrical, and uniform in diameter, and the support-roll bearings must impart no errors in rotation.

The work rollers are of hardened steel (85 Shore) or are hard chromium-plated. The support rollers should

be accurately adjusted and have their barrels gradually relieved at the ends, as the concentrated pressure from sharp-edged ends of support rollers can soon wear bright rings on work rollers which cause undesirable bands on the sheet.

The lubrication of the support and work-roller bearings must not be excessive, as any leakage of oil or grease causes the sheets to be marred by greasy spots or bands imprinted on them.

A cause of trouble with the backed-up type of roller-leveller is that solid particles picked up from the sheet itself are prone to adhere to the work rolls and cause a succession of objectionable small indents on the sheet surface. One way of eliminating these adherent particles is to wipe them off as often as necessary with a length of fine abrasive paper, folded over a wide strip of cardboard sufficiently long to pass right through the yoke of rollers, and pulled slowly from one side to the other as the rollers rotate.

Sheets are fed into these machines from a two-rail trestle or a flat-topped table and run out similarly. All stationary surfaces which may come in contact with the sheet must be of wood or plastic material, or faced with paper or cloth, and be kept free from dust, to avoid scratches.

One unavoidable effect of roller-levelling is the formation of a slight ripple at the ends of the sheets.

Typical sizes and duties of backed-up roller-levellers are as follows:

- (1) 23 work rolls $1\frac{3}{4}$ in. dia. \times 60 in. for sheet gauges 0.018 in.-0.048 in.
- (2) 17 work rolls $1\frac{3}{4}$ in. dia. \times 75 in. for sheet gauges 0.028 in.-0.080 in.
- (3) 17 work rolls $2\frac{1}{2}$ in. dia. \times 86 in. for sheet gauges 0.028 in.-0.125 in.
- (4) 15 work rolls $4\frac{1}{4}$ in. dia. \times 84 in. for sheet gauges 0.125 in.-0.250 in.
- (5) 11 work rolls 8 in. dia. \times 100 in. for plate gauges $\frac{1}{4}$ in.-2 in. thick.

Linear working speeds range from 30 to 120 ft./min. and are usually variable.

4. SHEET STRETCHING OR STRETCHER-LEVELLING

The most effective flattening machine for many qualities of flat sheets is the sheet-stretching machine, in which the sheet is gripped securely at each end uniformly across its width in straight grips and given a slight stretch of about $\frac{1}{2}$ -1% of the length.

Typical sheet-stretching machines have the following proportions:

Max. Width of Sheet	Max. Finished Sheet Length	Max. Sheet Thickness	Max. Force
4 ft.	15 ft.	$\frac{1}{8}$ in.	125 tons
4 ft.	50 ft.	$\frac{1}{8}$ in.	150 "
4 ft. 6 in.	16 ft.	$\frac{1}{8}$ in.	150 "
6 ft. 4 in.	18 ft.	$\frac{1}{8}$ in.	200 "
6 ft. 4 in.	22 ft. 6 in.	$\frac{3}{8}$ in.	400 "

The main features affecting sheet quality are: sheet handling, sheet gripping, sheet positioning, and extent of stretch. Sheets are generally placed by hand on the machine usually by turning over sideways on to the bed of the machine, clean, felt-faced saddles across the bed being provided to receive the falling

sheets without damage. With two men handling the sheets properly and curling them somewhat before lifting, there should be no damage, but with improper handling it is easy for the hands to make kinks in thin sheets, as in all sheet handling, and this must be avoided. Plates too heavy to man-handle must be slung on and off by crane.

The type of grip and its effectiveness are most important. In all cases, the grip body must be very robust and must not deflect appreciably under the force of stretching. For the narrower machines, it is simplest to have single-piece faces held to the sheet by hand-lifted toggle bars. In the simplest type of machine, the lower grip face is fixed to the grip body, and only the upper is engaged by the toggle bar. This means that, with some thicknesses of sheet, the grips cannot be in full register. It is preferable to have both grip faces engaged with geared toggle bars, and they should be adjusted to be always in full register. With these single-piece grips, it is essential that they are accurately fitted in their seatings so as to make uniform contact all across the sheet. With machines 6 ft. wide, it is preferable to have sectioned grips, brought into contact with the sheet by a flexibly connected common air cylinder, the grip sections sliding down inclined faces in the grip body, and each capable of an individual wedging action for getting full grip under the stretching force. Usually the individual action of each grip section is modified by there being a single-length grip blade fitted across the lot.

The stretching stress applied to the sheet must be adequate yet not too intense, and transversely uniform. This requires a sufficient longitudinal length of grip face (usually 2 in. is sufficient), as well as correctness of grip surface. Obviously, smooth grip faces could not apply sufficient force in the short length available, and serrated faces, with good sharp serrations pitched 8 to 12 to the inch, coarser for thick sheet and finer for thin, are suitable, provided they are clean and sharp and are absolutely uniform in transverse bearing. Additional oblique serrations for transverse restraint are sometimes favoured, also male-female indented grips for thin material. The teeth furthest from the ends of the sheet should bear less hard than the rest; otherwise they will tend to cause stress concentration and to initiate premature tearing of the sheet. The effectiveness of the grips can be reduced by the presence of oil on the sheet surface.

In regard to positioning of the sheet in stretching, it is important to arrange the sheet with its centre line coincident with the centre of each grip head. If gripped obliquely, or even off-centre, the tendency to tear in the grips is increased.

The extent of stretch is usually a matter for the operator's judgment. Some operators work solely by the appearance of the sheet, other supplement this by watching the pressure gauge, and releasing pressure when it has attained a value which experience has shown to be the safe limit. If the plastic stage is

insufficiently developed, flattening may be inadequate when the stress is released, even though the sheet has a flat appearance under stress. For this reason, reflecting aids are of little use to the operator.

The plastic stage usually indicates itself by a slight dulling of the sheet surface. If stretching is carried too far, irregular oblique lines, bands or patches, of the type of Lüder's lines, will develop, which spoil the sheet. In the case of aluminium-magnesium alloys, stretcher-strain markings of a more pronounced type, either the flamboyant or the oblique-band type, more readily develop and must be avoided, although with these alloys, the practice of prior roller-levelling or light planishing assists in avoiding this objectionable feature. If stretching is excessive, the sheet will tear from the side, either in the grips, or centrally, and be ruined. This is liable to happen quite unexpectedly in sheets of the harder-rolled tempers and thinner gauges.

The operation of stretching flat sheet is more complex than it appears, as a secondary effect of the existence of a longitudinal direct stress in the sheet is the co-existence of a compressive stress component at right angles to it, evidenced by the lateral in-gathering of the sheet into a slightly fluted or "piped" shape. Unfortunately, when these flutes develop, they usually remain after the release of stress and are sufficiently detrimental to cause rejection. The tendency to the formation of flutes is increased by transverse light-pressure areas in the grips, and therefore good fitting is essential, to ensure transverse uniformity of pressure, while cross-hatching the grips may assist to restrict lateral movement. Again, the lateral resistance of the sheet to fluting can be enhanced by increasing the moment of inertia of its longitudinal section, and this can be done to a small, but sufficient extent, by supporting its mid-length slightly above the level of the grips. This is sometimes found useful with thin sheets.

The harder-tempered aluminium-magnesium alloys, with a relatively high proof stress, do not respond to stretcher-levelling so readily as the temper-rolled pure aluminium, and aluminium-1½% manganese alloys; whereas heat-treated alloys, having a good degree of elongation, respond well to the operation.

5. SHEARING AND SAWING OF SHEETS AND CIRCLES

The final shearing or "re-squaring" of sheets is usually carried out on guillotine shears, although in some cases, machines with revolving rotary slitting cutters are used. The objectives are to cut the sheet to the required size with a clean-cut edge, free from bend or burr, and without damage such as scratches, indentations, or marks.

A disadvantage of rotary slitting knives is that when a sheet is fed through them, it does not always travel exactly straight, and its final edges may not therefore be quite straight; another feature of rotary knives is that they are more liable to cause slight bend, burr, or other irregularities than do straight shear knives.

An interesting application of a rotary shear is the type where one rotary knife is arranged to traverse along the length of an opposing, long, fixed shear blade. Advantages of this are that the very long lengths can be cut on a comparatively light machine, and that the edge can, if desired, be cut chamfered, but disadvantages are that the off-cut on the rotary side curls and becomes unusable.

In the ordinary, straight guillotine shear, it is usual for the moving blade, usually the top one in finishing shears, to have a longitudinal rake. The greater the rake, the less the force required for cutting, but the greater the tendency to impart some small surface-curvature to the sheet, especially on the off-cut side.

For best-quality shearing, a blade rake of 1°-1½° is satisfactory; a rake of 3° is used for heavy work, and this may impart a slight bend. Some of the hardest precipitation-treated alloys are likely to appear brittle on shearing with a high blade rake of 3°, and better results on these materials can be obtained with the 1½° rake.

The avoidance of a burred edge depends on having the blades truly ground to a sharp edge, and accurately set to a suitable uniform clearance—if in contact, of course, they will rapidly wear. The horizontal surfaces can be ground square, or with a few degrees of clearance angle, i.e. up to 4°. The vertical (overlapping) surfaces are usually ground with a clearance angle of up to 10°, 6° being usually satisfactory. Inter-blade clearances must be small for thin sheets and larger for thick sheets, as follows:

For ½ in. plate and over	0.008 in. inter-blade clearance.
" ¼ in. "	0.004 in. " " "
" ⅛ in. sheet	0.003 in. " " "
" 0.036 in. sheet	0.002 in. " " "
" 0.018 in. "	0.0015 in. " " "

If too great an inter-blade clearance is used, a burr forms on the edge of the sheet.

To maintain the cutting edge, the shear blades are of medium hardness, a Shore hardness of 75-82 being satisfactory. An occasional wipe with a paraffin rag assists the maintenance of a good cut.

If the shear blades are ground sharp and true and correctly set, it is possible to shear thin sheets satisfactorily in packs of two, but if the blades are not accurate, shearing in packs results in burred edges.

The cutting of a sheet to correct size depends mainly on the correct measurement settings by the operator, whether shearing to scribed lines on the sheet, or shearing against stops and squaring arms. However, especially with high-rake shears, there is a tendency for the descent of the blade to throw the sheet out of its setting, resulting in incorrect dimensions and a curved edge. With thin sheets, this can be prevented by pressure from the operator's hands holding the sheet to the shear table to prevent its movement. With thick sheets and plates, greater force is required for holding down, and is provided by cam- or air-operated, or spring-loaded, hold-down rams; to avoid marking, these should be faced with a smooth resilient material and kept clean, and the

speed of descent of the rams and the force exerted should both be restricted to the minimum necessary.

To keep sheets out of contact with the shear blades, except when cutting, plastic or cardboard sheet, fixed to the shears bed, should stand about $\frac{1}{16}$ in. proud of the bottom blade, and a suitable plastic, wood, or fabric protection for the tables and top guards, if kept clean, prevents scratches.

For the more expeditious and consistently accurate shearing of sheet in quantity, ganged guillotine shears are now sometimes used, having a first pair of side-cutting guillotines followed by a second pair for end-cutting. Adjustments of the position of the shears units for size are made by power-driven screws; the dimensions can be seen on scales, but should nevertheless be checked by measurement on the sheet itself after shearing. To convey sheets through the side-cutting shears, rubber-faced conveyor link-belts are provided, at both top and bottom. It is necessary that the conveyor pads be accurately adjusted to convey the sheets about $\frac{1}{8}$ in. clear above the lower blades, and the pads of the upper belts must be in accurate register with those of the lower, and pressing only lightly. All pads must be clean and free from grease.

A composite arrangement of a pair of circular shearing knives for side-cutting and a transverse guillotine shear for end-cutting is simple, but inferior to the ganged guillotines in respect of quality of cut, and of consistent straightness and squareness.

For thick plates of the order of $\frac{1}{2}$ in., which may be above the capacity of available shears, good straight-cutting is possible on travelling milling-saw machines with soluble-oil lubrication. This process is slower than shearing and produces swarf; it is therefore more costly.

For curved or straight surfaces, cutting may be reasonably well carried out on high-speed wood-cutting bandsaw machines, the saws having sharp, well-set teeth of about $\frac{1}{4}$ in. pitch for the thicker plate and being well guided, tallow or oil lubricant being applied to speed the cutting. The cut is hand-guided and cannot be expected to have an accuracy closer than about $-0 + \frac{3}{16}$ in.

6. TRIMMING AND SLITTING COILED STRIP

The principal final processes for coiled strip are edge trimming and, frequently, slitting into multiple widths; both are combined with rewinding into finished coils.

This operation is carried out on a slitting machine, the main element of which consists of pairs of circular cutters or knives set close axially with a small diametral overlap (clearances given later) and mounted securely and accurately on revolving top-and-bottom arbors, which must be true running in error-free bearings.

The cutters or slitter-knives are of hardened shear steel in the form of flat discs (splined inside), or rings mounted on hubs, a usual hardness being 70–75

Shore. The flat-disc type of knife is threaded over the spline-shaft arbor and located by accurate spacer sleeves, the assembly of knives and spacers being clamped up tight together between an integral shoulder at one end of the arbor and a nut at the other end. Fine adjustment of axial distance between knives is made by the insertion of shims, or with the use of screw-type spacers. The hub-mounted type of knife is usually made to slide independently along the arbor and can be locked up on it in any position by clamping screws or wedges. This type of knife has the advantage that it can be more quickly readjusted for new widths than the spacer type, but the clamping must be such that the knives run true. The knives in all cases must be precision-ground with fine finish, both on faces (which must be square, or slightly relieved) and cylindrical surface, and must revolve absolutely free from wobble or eccentricity. Felt wiping-pads set in contact with the knives, lightly oiled to provide a film of lubricant, assist in maintaining good cutting and wipe off particles.

When strip passes through the slitter knives, it is divided by each knife-pair, the strip on one side of a cut being moved downwards slightly by the upper knife, and that on the other side upwards by the lower knife. The widths of strip between knives have a tendency to press hard against the cutters and to be pulled round with them as they revolve. With very thin strip, the longitudinal working tension in it may be sufficient to pull the strip clear of the knives, but with thicker material it is preferable to provide a positive means of immediate stripping from the knives, and this generally improves the quality of the slit edge at all gauges. If this is not done, the strip may be plucked away from the knives periodically, and this may result in a waved or faintly crimped edge. The strippers can be flat bars of wood or smooth steel, cloth-faced for preference, fitting within $\frac{1}{32}$ in. of the knife face, and capable of vertical adjustment to avoid forcing the strip down hard on the opposing knife and causing a knife-mark on it from the spare edge of that knife. This can be prevented by providing another "wood" between the inner knives to hold the strip out of contact with their peripheries except at the point of cut. An alternative means of stripping is to have rubber sleeves over the arbors or spacer sleeves.

The best method of pay-out for the incoming coil is a cone decoiler, with which pressure indentation of the strip in paying off is avoided, and which is provided with an adjustable brake to give sufficient tension for the rewind. The strip passes to the slitter head through plate side-guides, roller guides being useless with thin strip. To counteract lateral displacements in the unwinding coil which may be caused by earlier winding irregularities, a means of making lateral correction of the position of the coil is desirable, and this can be made automatic with photo-cell or air-jet signalling.

It is necessary to keep the strip flat as it runs through the slitter in order to achieve the correct

width. Multiplication of the stripper "woods" is effective for this hold-down, but a felt-faced hold-down pad on the ingoing side across the whole width, under just sufficient pressure to maintain flatness, is often of advantage. The strip can run over pass-line rollers before and after the slitter, and with thin strip this is often sufficient to maintain the lateral flatness of the strip under its tension.

The rewinding of the coil after slitting is done on rewind reels or drums, which must run true and be capable of collapsing for the purpose of stripping.

Coil-slitting and rewinding machines can be arranged to run with driven or non-driven knives ("pull-through" slitters). In either case the rewind reel must, of course, be driven. With driven knives, the speed of the rewind reel must vary to suit the speed of the knives. Positive drive to the knives and a slipping drive to the rewind reel is one satisfactory means for achieving this; or a variable electric drive may be used. With the non-driven "pull-through" knives, there is no problem of speed-matching, as only the reel is driven, though this can well have a variable speed for achieving the best slitting and inspection conditions.

As with strip-rolling mills, the rewinding reels or drums must be truly cylindrical, and the gripping slot must be such that it will not leave a "drum-mark" in the strip when subsequently unrolled. For slitting, sometimes called "gang-slitting", where two or more coils have to be rewound, individual coils, if rewound on a single reel, must be separated by smooth-edged, true-running, sheet-metal spacing discs about $\frac{1}{16}$ in. thick, threaded on the reel, and larger in diameter than the coil. The edges of the strip will be in contact with the revolving disc edges, and it is possible for damage to occur. Some users recommend placing the reel well away from the slitter knives to facilitate "fan out", but others find that a reel close to the knives gives a better wind. Twin rewind reels, one following the other, are useful for multiple slitting, alternate coils being rewound on alternate reels; it is necessary that tension and speeds be made equal on each reel. Coils may also be rewound on spools threaded on the rewind reel or mounted between driven chucks.

For special flatness of product, a backed-up roller-leveller can be installed in the line, preferably after the slitter, the leveller being driven at a controllable speed. The slitter and reel are also driven at a controlled speed and are provided with means for indicating the tension in the strip at intervals.

The objectives in slitting are to recover a tight and true-wound coil of the required width, free from indentations or scratches, and with clean-slit edges free from imperfections such as wave, burr, or crimping, while all strips must be straight.

Damage to the coil must be prevented by careful lifting by C-hooks, slings, or fork trucks. Coils should not be rolled over rough floors. The formation of indents in the strip arising from particles adhering to pass-line rollers is prevented by light wiper pads on those rollers.

Tightness of winding requires sufficient tension in the strip, which is determined by the resistance of the cone brakes, the added friction of the wiper pads, and the resistance of slitting, all balanced by the opposite pull of the rewind drum drive.

Trueness of wind is assisted by pay-off in an unvarying line, with correction of previous winding irregularities in the paid-off coil, as mentioned earlier. Continuous correction of the centring of the coil also maintains equal offcuts on each side of the coil, which is important, as it is usually defective or distorted metal that is cut off.

Straightness of strip cannot be controlled by the slitting machine. Strip that is curved before coming to the slitter for trimming will be similarly curved after rewind. Therefore, straight-rolling is necessary, the usual limits of tolerance being 1 in. departure from the straight on 10 ft. length for general work, and $\frac{1}{4}$ in. on 10 ft. for high-class work. To finish with straight-trimmed coils, they must be straight after rolling in the strip mill. To finish with straight-slit coils requires flat—as well as straight—rolling. When coils are slit into ribbons, it is not uncommon for the two side ribbons to become convex relative to the centre, as seen from above, owing to rolling strain. This is corrected by rolling flat rather than with an under-pinched slack middle and is also improved by a generous edge-trim of about $1\text{--}1\frac{1}{4}$ in. per side.

To obtain good cut edges, the knives must be ground true and of fine surface and set appropriately in mesh, or diametral overlap, e.g. 0.015 in. for thin material (0.010 in. thick) and 0.060 in. for $\frac{1}{8}$ -in.-thick strip. The axial clearance between the knives of a pair varies from 0.001 in. for thin gauges (0.010 in.) to 0.003 in. for $\frac{1}{8}$ -in.-thick strip.

7. PUNCHING OF CIRCLES

The punching of circles on short-stroke blanking presses is more frequently carried out with automatic feed on coiled-strip material than with hand-feed on flat sheet, the use of the latter being usually restricted to the thicker gauges over 0.064 in. For strip, a double roller feed is satisfactory, or a double moving-gripper feed. Pay-out arrangements for the coil may be from a driven-roller coil-box or non-driven cones with driven pinch-rollers, but in either case a loop must be pulled out continuously and maintained, as the decoiler must work continuously and the punch requires intermittent rapid movement, which it gets from the automatic feed.

For the blanking tools, unhardened medium-carbon steel is satisfactory and can be fullered up for regrinding to size. The punch is parallel-sided, and is ground with a slight relief of 2° or 3° on the flat face. The die may be flat or have a similar relief on its flat face, and its cylindrical interior face is relieved 3° or 4° to permit the circle to fall clear, there being a $\frac{1}{16}$ -in. length of parallel (covered by the stroke of the punch) to assist in the retention of clearance. Radial clearance between punch and die ranges from 0.002

in. for the thinnest gauges of 0.018 in. and smaller diameters, up to 0.008 in. for the thickest gauges (over 0.080 in.), and larger diameters (up to 24 in. for instance).

When coiled strip is fed, it is preferable to take out the coil curvature in the strip before punching, and this is done by passing between a 3- or 5-roll undriven leveller, with adjustable penetration and preferably with rubber-covered rollers.

8. FINAL ANNEALING OF FLAT SHEET, CIRCLES, AND COILS

This subject has been dealt with in detail by King and Turner¹ and also by Paton,³ in whose paper the principles of the processes and plant were fully described. The following notes on the methods and the reasons underlying them are supplementary.

Final annealing is necessary for material required in soft temper, such as coiled strip for re-rolling into foil, and flat sheet and circles where a drawing, stamping, or stretch-forming operation involving a substantial stretch has to be carried out, for which high elongation is required in the sheet.

It is usual to slit and rewind coiled strip to final width before the anneal and there is no further rewinding after anneal as a rule, although this can be done if the slitting is carried out at the same time so as to give a straight-walled rewind. It is also usual to punch circles and shear flat sheets to their finished size before the final anneal, as handling of the annealed sheets through these operations without damage is less easy than before anneal, and the punching or shearing operation gives a slightly turned-up edge on annealed pure aluminium or the aluminium-1½% manganese alloy.

Final annealing is usually carried out in closed oven-type furnaces with internal electric heaters and fan circulation of the air, as these are usually found to be the cheapest in operating cost, and reliable in temperature control and uniformity.

Conveyor-type furnaces with continuously moving belts, which have been described by Staples,⁴ are sometimes used for flash-annealing products when a rapid rate of heating is desired, the sheets or circles being loaded singly or in small piles on the conveyor belt, which usually has the form of a driven steel-wire-mesh mattress belt, or a belt composed of several endless stranded steel wires or steel ribbons, of heat-resisting quality. A circulating atmosphere is used in the heating chamber to increase the rate of heating, and also in the subsequent cooling chamber to increase the rate of cooling, but in neither case should the rate of circulation be high enough to move the charge on the conveyor and cause abrasions. This type of furnace is higher in operating cost than the batch-oven type.

The highest possible rate of anneal is given by immersion in a molten bath of lead or nitrate of soda. Both these can be used at 350° C., but the metal would require pushing down in the lead, while the nitrate of soda has the disadvantage of the high cost of

drag-out loss and of the subsequent washing and drying processes.

The annealing of coils in either of the above two types of rapid-annealing furnace would not be feasible, but it would be possible, at extra operating cost compared with the annealing of wound coils, and with some complications such as joining coils, to pay the coils out continuously in single strip form through a furnace for the purpose of "flash" anneal and to rewind to coil afterwards.

Flash-annealing is mostly used on the aluminium-1½% manganese alloy, which is prone to the formation of a somewhat coarse grain-size when annealed slowly; however, if properly homogenized cast blocks are used, even slow annealing gives quite good results, especially if, with sheets, the stack height is limited to 2 or 3 in. Some demands for ultra fine-grained, strong-alloy sheet can be met only with an accelerated anneal, either in flash-anneal furnaces or salt-baths.

The objects of final annealing are to impart maximum softness and ductility, a fine grain-size, and generally uniform properties.

To impart maximum ductility to the metal requires heating to a temperature at which work-hardness rapidly disappears, and recrystallization takes place. Although the rate of cooling does not have a great effect on the ductility of pure aluminium and its binary alloys, nor even on the heat-treatable alloys when cooled from minimum annealing temperatures, a slow rate of cooling is generally adopted; this has the advantage of producing greater ductility than rapid cooling in the case of heat-treatable alloys annealed somewhat above the minimum temperature. As the rate of rise of temperature follows an exponential curve, it would take considerable time for a coil of metal or a pile of sheets to attain a desired temperature if surrounded only by hot air at the desired annealing temperatures. For that reason, the temperature of the furnace atmosphere is maintained higher than that desired in the metal. This results in greater variation in temperature in the metal being annealed, and, for that reason, the "temperature head" should be restricted in the annealing of heat-treatable alloys.

To anneal pure hard-rolled aluminium, the metal is brought to about 360° or 370° C., at which temperature it is allowed to remain for ½ hr. to effect complete softening. To attain this temperature in heavy coils weighing 1 ton or more, in a time-cycle of 6-8 hr., requires the use of a furnace-circulated-atmosphere temperature of about 530° C. The aluminium-1½% manganese alloy requires a slightly higher temperature. Aluminium-magnesium alloys are annealed at a somewhat lower furnace temperature to reduce darkening of the surface colour. Heat-treatable alloys are also annealed at a somewhat lower furnace temperature to avoid excess metal temperature and the risk of any subsequent age-hardening. The times required are found by trial and will depend on the wall thickness of a coil and on the height of a stack of sheets.

Typical annealing conditions are shown in Table I.

The factor of greatest importance in the control of grain-size in pure aluminium sheet and low-alloy sheet is the percentage of previous cold reduction, as demonstrated in the classical work of Carpenter and Elam.⁵

TABLE I.—*Typical Annealing Conditions for Various Materials.*

Material	Furnace Temp., °C.	Metal Temp. Attained, °C.	Total Time, hr.	
			Coils	Sheets
Pure aluminium . . .	530	360-400	6-8	4-6
Al-1½% Mn alloy . . .				
Binary Al-Mg alloys . .	440	340-350	6-8	6-10
Heat-treatable copper-bearing alloys of L72 type	400 *	350	7	6-8
Heat-treatable zinc-bearing alloy of D.T.D.687A type .	420 *	360	7	5-7

* Softness is improved by cooling for 1 hr. in the muffle after annealing.

A cold reduction of about 66-70% should be given in the preceding processes as far as practicable, to promote a fine grain-size after anneal.

In the case of the alloys, such high cold reductions are not always practicable nor always necessary to ensure a sufficiently fine grain-size, although the high reductions do show a small advantage in respect of this and of other properties.

A secondary factor affecting grain-size in several of the alloys is chemical composition. The presence of manganese as an impurity in commercial pure aluminium sheet has a detrimental effect on grain-size after anneal, and this element is best kept very low. High iron (0.6%) and low silicon (0.2%) are favourable to a fine grain-size.

In the case of the aluminium-1½% manganese alloy, cold reduction alone will not ensure a fine grain-size after annealing. Homogenization of the cast block (or "rolling ingot"), i.e. a diffusing soak at a temperature approaching 600° C., before hot rolling, is therefore essential, and further advantage can be obtained from an accelerated final anneal, as mentioned above. With ordinary box-type furnaces, a useful accelerated anneal can be obtained by limiting the stack-height of sheets to 3 in.; the annealing cycle can then be completed in 2-3 hr., a time which gives a reasonably fine grain-size, acceptable for most purposes.

A simple method of grain-size assessment devised in 1943 by H. W. L. Phillips and E. E. Spillelt, of The British Aluminium Co., Ltd., and confirmed by P. C. Varley in 1947, is based on the appearance of the dome produced in the Erichsen indentation test. Arbitrary numbers are given to certain grades of roughness of the dome, as assessed visually, the coarsest being designated 1, and the finest 8. Standard samples are kept at hand for checking

against current assessments if necessary, but those using this system rarely have to make such reference. The system makes for simplicity of inspection, reporting, and recording.

The arbitrary Erichsen numbers correspond with the following metallographic grain counts:

Erichsen No.	Mean Grains/mm. ²
1	250
2	300
3	400
4	550
5	800
6	1200
7	1750
8	2700

In practice, a grain-size of Erichsen 5 or 6 can be produced in the aluminium-1½% manganese alloy with block homogenization, and is satisfactory for most purposes. If homogenization is omitted on continuous-cast blocks, the grain-size is 1 or 2, which is too coarse for press-work, though usually acceptable for folding or corrugating. The control of iron and silicon content, as for pure aluminium, is desirable for attaining the finest grain-size, and the presence of about 0.1% copper is generally found to give a slight refining action.

Freedom from burnt-oil stain after annealing is greatly assisted by requiring the rolling mills to deliver the strip as free as possible from rolling oil. As has been stated previously,⁶ increased annealing temperatures and times help to give a stain-free product, but nevertheless it is desirable to keep the oil to a minimum. The use of an oxygen-free atmosphere is also reported to facilitate stain-free annealing.

Adhesion between sheets in stacks is sometimes troublesome and can be alleviated, if it occurs, by lightly dusting the sheets beforehand with talc powder.

Sheets for annealing in box-type furnaces, if built in neat stacks on a flat-surfaced stillage, can be annealed to a sufficiently flat shape without requiring previous special flattening.

Circles are stacked and annealed in flat steel, shallow-sided, stillage trays.

Coils, if with open bores, can be annealed while standing up on one end. This method tends to give oil stains at the bottom flat end. Alternatively, they can be threaded horizontally on pipes, held on carrier frames. Coils wound on spools are similarly annealed.

Blisters make their appearance at the final anneal stage. The cause of them is the existence of gas segregations or inclusions in the metal right from the cast-block stage. The effect of annealing is to expand the gas and so lead to the blisters. These are thus not primarily due to the final process, and are not generally regarded as capable of control at that stage, although certain dips or furnace atmospheres have been reported as potentially beneficial.

A method of obtaining intermediate tempers for

strip and sheet that is coming into wider use, as an alternative to temper-rolling with a controlled appropriate reduction from annealed strip or sheet, is the process of "partial annealing" of hard-rolled strip or sheet, as Paton³ terms it, or "temper-letting-down" as it is called in the authors' Company, or "temper-annealing" as it was designated by King and Turner⁷ (to whose paper reference should be made for fuller information), or "heat-tempering" as it could also be called.

This "temper-letting-down" process is based on the fact that at temperatures lower than the recognized annealing temperature, the rate of loss of work-hardness is slow and generally fairly linear, so that it is possible to stop the heating after a pre-determined time and thus to give the desired temper with reasonable certainty. Large masses of metal, such as big coils or big stacks of sheets, cannot be brought to the "letting-down" temperature quickly, and in the period of gradual rise in metal temperature some reduction of properties takes place, continuing more rapidly as the requisite temperature is approached. The size of coil or stack affects the time. Generally speaking, however, by using a contact pyrometer to indicate the temperature of the load and by giving the load a definite time at the temperature, say $\frac{1}{2}$ hr., the properties resulting come sufficiently close to requirements. The rate of loss of work-hardness is roughly the same for all initial degrees of work-hardening of a given metal or alloy; thus, to finish with a uniform temper, it is desirable to start with a standard degree of work-hardening for each material.

The conditions of the temper-letting-down process are empirical, and each user has to find out his own best conditions by trial.

TABLE II.—*Conditions for Temper-Letting-Down or "Temper-Annealing" of Various Materials.*

Material	Desired Temper	Starting Temper	Temper-Letting-Down Conditions		
			Desired Temperature for Metal, °C.	Time at Temp., hr.	Approx. Total Time Cycle, hr.
99% pure aluminium	$\frac{1}{2}$ -hard $\frac{1}{4}$ -hard	Hard-rolled (no anneals)	230	} 3	12
			235		
Aluminium-11% manganese alloy	$\frac{1}{2}$ -hard $\frac{1}{4}$ -hard	Homogenized Hard-rolled (no anneals)	290	} 3	12
			295		
Aluminium-21% magnesium alloy	$\frac{1}{2}$ -hard $\frac{1}{4}$ -hard	Hard-rolled (after anneal) 50-55% reduction.	175	} 1	7-8
			245		
Aluminium-31% magnesium alloy	$\frac{1}{2}$ -hard $\frac{1}{4}$ -hard	"	110	} 1	7-8
			235		

Examples of temper-letting-down conditions that are in use, applied to the hardest mill temper normally produced, are given in Table II.

The combination of physical properties in temper-let-down sheet is usually somewhat different from

that in temper-rolled sheet. For the same tensile strength in the two cases, the proof stress is lower and elongation higher for temper-let-down sheets. Nevertheless, it is sometimes found that the temper-rolled material has somewhat the better bending and flanging behaviour. An advantage found for temper-let-down low-magnesium aluminium-magnesium alloy sheets is that they are more responsive to the flattening processes of roller-levelling and stretching than are temper-rolled sheets. When producing temper-let-down sheet, it is sometimes preferred to bring the material, if in coil form, into sheet form first, as there is less risk of damage by scratching in this way; moreover, the flatness tends to be slightly better, any effect of "coil spread" in the letting-down process being avoided.

The use of the temper-letting-down method has sometimes an economic advantage over the temper-rolling process, when it is possible for the extra rolling pass necessary for temper-rolling to be avoided.

III.—HEAT-TREATMENT OF STRONG ALLOY SHEET AND COIL

The heat-treatable light alloys still follow closely the original alloy invented by Wilm⁸ in respect of composition and process of solution-treatment and room-temperature ageing, the British L.3 family of aircraft sheet specifications being close to the original alloy. The essential components of this alloy are copper 4, magnesium 0.6, and manganese 0.6%, with a base metal of commercial 99% purity aluminium. The American 24S type of alloy represents a small advance on this, the amounts of the alloying elements being increased to copper 4.6, magnesium 1.5, and manganese 0.6%, and the British D.T.D.390 aircraft sheet alloy is somewhat similar. The foregoing alloys are given solution-treatment and room-temperature ageing to develop their full strength; precipitation-treatment or artificial ageing at a somewhat elevated temperature gives no marked benefit to the L.3 and D.T.D.390 alloys, though it is applicable to 24S. In Britain, in the last decade, very similar alloys have been developed, which undergo not only similar room-temperature ageing, but also a very substantial increase in proof stress on precipitation-treatment; the aircraft alloys to Specifications L.70-L.73 are of this type, approximately copper 4.4, magnesium 0.7, silicon 0.7, manganese 0.6%.

The aluminium alloy of highest strength, namely that covered by aircraft sheet alloy D.T.D.687A, corresponds to the American 75S, and follows earlier alloys of this type developed in Germany (by Goldschmidt and VLW companies) and in America by Fuller and Basch. The main components are about 6% zinc and 3% magnesium, with about 1.3% copper, and this alloy has no advantage unless its properties are developed to the full by precipitation-treatment following solution-treatment.

Another type of alloy that is now prominent in commercial work, though not in aircraft construction on account of its inferior strength, is one of simpler composition and greater ease of manufacture, possessing medium-high properties, namely an aluminium alloy with Mg_2Si as its hardening constituent (from $\frac{1}{2}\%$ to about 1% of each element) developed earlier, particularly in Switzerland, for general constructional use. It is used widely both in the solution-treated and in the precipitation-treated conditions under the B.S. specifications HS10W and HS10WP, respectively.

King and Turner¹ have dealt with several factors in the heat-treatment process, while Paton³ discussed equipment on a wide scale.

1. THE SOLUTION-TREATMENT OF SHEET

Solution-treatment consists of heating the alloy at a temperature 10° – 15° C. below the solidus temperature (i.e. at as high a temperature as can safely be used without risk of incipient fusion) for sufficient time to permit full development of its properties, followed, without appreciable loss of temperature, by rapid quenching in cold water.

The temperatures of solution-treatment are laid down in the relevant specifications and are approximately 500° C. for the high-copper alloys, and 465° C. for the D.T.D.687A type of alloy.

The soaking time at the solution temperature, though not specified, is an important factor. If it is too short, solid solution within the alloy is not completed and the properties are inferior. If too long a time is allowed at the solution temperature, the properties do not suffer, but undesirable diffusion of copper through the pure aluminium cladding sheets may occur in clad material. The appropriate time of solution-treatment, which must be determined by trial, has been found to vary substantially with gauge.

The time interval between withdrawal of the sheet from the heat-treatment furnace and quenching must be as short as possible to avoid loss of temperature, and varies from about 4 to about 20 sec. The quenching water is required to be held to a maximum of 40° C. in some specifications.

The quench tanks must be placed as close as possible to the furnaces to keep down the time of transferring the load. In the case of air-circulation furnaces, it is a common practice to place the furnace aloft, so that the quench tank can be fixed or brought into place below it to receive the load of sheets in a very short time of about 3 or 4 sec. With salt-baths, the quench tanks must be set close beside the baths, with only walking space between. A broadside-on position gives a shorter path of travel for the load and lower quench intervals than does an endways-on position.

The types of furnace used for the solution-treatment of aluminium alloy sheets are the nitrate salt-bath and the air-circulation furnace. Both may be

heated by gas or electricity, but in either case, very close control and uniformity of temperature are necessary. This can be readily achieved in bottom-heated electric salt baths of the Kaercher type, and a temperature range no greater than 3° C. has been observed in these, whereas a range of 10° C. is permitted by the aircraft sheet specifications. In air-circulation furnaces, the temperature variation inclines to be rather higher.

For charging into the solution-treatment furnace, sheets are rested on, or suspended from, mild-steel carrier frames. These may have central vertical columns with transverse bottom sills affixed, on which the sheets may be set close together and secured from falling outwards by vertical rods placed in an external position after loading; alternatively, vertical rods may be set between each sheet or pair of sheets to ensure more open spacing.

Another method for thick sheets and plates is to rest sheets on a sufficient number of bottom hooks formed at the end of long rods whose upper ends are hooked to the upper lifting frame, this requiring less weight of steel to be heated than in the case of bottom-sill frames. A further method of sheet suspension, especially suitable for sheets $\frac{1}{8}$ in. thick and less, is to support the sheet by clips at the top edge, these clips being suspended by short hooks from an upper lifting frame, which is not immersed in the case of salt-baths. The clips are usually of mild steel and of robust dimensions, and the gripping faces are horizontally serrated to increase the vertical hold. Application of the grip may be by wedges hammered in and out, or by screws turned by a separate box-spanner key; in the latter case, a loose steel serrated plate moved in front of the screw is of advantage in increasing the area of grip. Clipped sheets must be supported at a regular distance apart, 2 or 3 in. being satisfactory for the general run of sheets.

The quality of sheets in solution-treatment may be impaired by abrasions or scratches caused by lateral movement due to thermal distortions in the rapid heating or cooling, or by fluttering in air-circulation furnaces, which should be minimized by suitable air-flow conditions. There may also be irregular bulges in thin sheets, due partly to sudden heating by the salt and partly to local steam pressure in the quench, and these bulges, or "sprockles" or "crockles" as they are termed in various localities, are difficult to obliterate completely in the subsequent flattening operations. Regularly spaced sheets of reasonable initial flatness and suspended by clips are usually found to give better results in these respects than sheets that are treated in a close vertical pack supported from the bottom, while coils suffer less than flat sheets.

The soaking time in the heat-treatment furnace depends on the gauge, as mentioned earlier, and air-circulation furnaces are found to require longer in heating than salt-baths. Again, some specifications require longer times than others. Examples of current practice for treatment times are given in Table III.

TABLE III.—*Examples of Solution-Treatment Conditions.*

Gauge, in.	Minimum Heating Times, min.			
	Specification D.T.D. 546X, B.S. L73 (Solution- and Precipitation-Treated)		D.T.D. 687A (Solution- and Precipitation-Treated)	
	Composition: Cu 4.4, Mg 0.7, Si 0.7, Mn 0.6%		Composition: Zn 6, Mg 3, Cu 1½%	
	Salt Bath	Air Furnace	Salt Bath	Air Furnace
0.020 and under	12	13	6	7
0.036	17	20	10	12
0.048	19	23	15	18
0.064	21	26	15	20
0.080	23	29	15	25
0.128	25	33	15	35
0.250	30	50	20	50

Temperatures of solution-treatment are as follows:

D.T.D. 390, B.S. L. 38 . 495° C. D.T.D. 610B, 546B . 510° C.
D.T.D. 610x and 546x } 505° C. D.T.D. 687A . 465° C.
B.S. L70-L73
HS10W and HS10WP (Al-Mg-Si) . 520° C. to 560° C.

It is possible to solution-treat the aluminium-magnesium-silicon alloy (HS10) at a temperature higher than 520° C., up to 560° C., with some increase in strength, but the former is the highest temperature at which nitrate salt-baths can safely be worked; treatment at 560° C. requires the use of an air furnace.

It is desirable that before heat-treatment the sheets should be practically free from rolling-oil stains, films of any sort, dirt, and water stains, for these may subsequently give rise to grey stains. In general, the colour of sheets from air-circulation furnaces is somewhat superior to, and more uniform than, that obtained from salt-baths. Where sheets happen to be in contact in salt-baths, there is a tendency for grey patches to develop. The use of 100% sodium nitrate in salt-baths has been found to be satisfactory, and sheets of good colour can be obtained. Experience, when adding 10% sodium nitrite to protect the tank, is that the surface colour is not so good as with 100% nitrate. After the sheet leaves the salt, it is essential to remove every vestige of the latter, and it is good practice to leave the charge undisturbed for 5 min. in the quench tank so that all the salt may be completely dissolved before transferring the load of sheets to the clean-water wash tank. In the case of unclad copper-bearing alloys of the L.3 or L.70 type, the colour after heat-treatment is darker than in the case of the clad alloys. In the case of unclad aluminium-magnesium-silicon alloys of the HS10W type, the colour is sometimes inclined to be grey or patchy. This can be alleviated by utilizing a low concentration of nitric acid (about 0.2%) in the quench water and leaving the charge in this for 5 min., or longer if possible. Protection of the steel tank by a suitable paint is necessary for this treatment.

The solution-treated sheets are particularly prone to develop scratches if they slide over one another or over other metal surfaces, as they are dry and unlubricated, and have become considerably distorted during quenching. Special handling care is therefore needed to maintain a high quality, and interleaving the sheets with paper assists in this.

2. FLATTENING OF SOLUTION-TREATED SHEETS

For sheets thicker than 0.064 in., the first flattening operation after solution-treatment is planishing through polished sheet rolls, usually of the old hand-mill type. One run is usually enough to take out the distortions sufficiently to permit further flattening. The effect of planishing is to increase the proof stress by about $\frac{1}{2}$ ton/in.² and slightly reduce the elongation, but all property requirements should still be met. Thinner sheets may be planished, or alternatively they can be given their first flattening pass through a backed-up roller-levelling machine, as described earlier. The avoidance of indentations from these machines must be specially watched. This type of machine may be found preferable to planishing for thinner sheets, as a good flat sheet is obtainable which is more amenable to further flattening. The second flattening process is carried out on stretching machines, as already described, and since the solution-treated sheets have a fairly high ductility, an adequate degree of stretch for good flattening is obtainable without fracture. Two impairments which come by overstretching are, however, to be avoided, namely stretcher-strain marking and longitudinal fluting or piping; the latter is more easily avoided if the sheet is smoothly supported from below, slightly above the line of stretch, so that its resistance to the lateral contraction, which causes piping, is increased.

Adequate stretching of thick sheets and plates that are to be subsequently machined on one surface reduces the distortion resulting from one-sided stress release on such machining.

In certain cases, where a sufficient flattening by stretching is not obtained, or where piping has occurred, it is advantageous to give a final run through a roller-leveller; before doing so, however, it is preferable to shear off the stretcher grip marks from the ends of the sheets, as otherwise loose particles from these may contaminate the leveller rolls and cause indentations.

As sheets harden rapidly shortly after solution-treatment, to obtain maximum flatness it is advisable to flatten as quickly as possible after the quench process, even to the extent of not fully completing the drying beforehand. For this reason, also, drying at room temperature rather than in ovens is preferred.

3. PRECIPITATION-TREATMENT OF SHEETS

The effect of precipitation-treatment, where it is applicable, is to increase the proof stress considerably, e.g. from a minimum of 15 tons/in.² in sheet to B.S.

specification L.72 before precipitation, to a minimum of 21 tons/in.² for L.73 after the process. (The ultimate tensile stress is increased to a less degree, i.e. from 25 minimum to 27 tons/in.²). Consequently it is essential for all flattening processes to be completed before precipitation-treatment.

The process is carried out in oven-type furnaces having air circulation, with indirect gas, or direct or indirect electric, heating and with close and uniform control of temperature. The temperatures to be used are low and are shown in Table IV. The time required is not specified and has to be found by trial. Normally, minimum times are adopted for economic reasons and additional time usually has a favourable, not a detrimental, effect. A total cycle time can be arranged, or a time measured from the attainment of the minimum required precipitation temperature by the metal as indicated by a pyrometer in contact with

TABLE IV.—*Precipitation-Treatment Temperatures and Times for Sheets.*

The overall cycle time is usually about 24 hr.

Specification	Required Precipitation Treatment Temp., °C.	Time Allowed (hr.) After Metal Reaches Min. Specified Temp.
D.T.D.546x (B.S. L73)	175 ± 5	5
D.T.D. 687A	135 ± 5	8
HS10WP	175 ± 5	6

it; in this latter case, of course, a considerable degree of precipitation takes place before the minimum temperature is attained. Times and temperatures used are given in Table IV.

4. SHEARING, MARKING, AND OILING OF HEAT-TREATED SHEETS

The last operation is shearing and this is carried out as described above (p. 203).

It is required that sheets for aircraft construction be over-all-marked with the specification number and maker's mark. This can be done on offset roller-marking machines with changeable soft-rubber type, using a very quick-drying and non-corrosive marking ink. To avoid indenting thin sheets, excessive pressure by the type rollers must be avoided. For sheets thinner than 0.018 in., it is helpful to place a thicker sheet below the sheet to be marked. It is also usually required by users that the sheets be delivered oiled, with an approved oil, usually a light mineral oil with lanoline admixture, as a precaution against corrosion in storage. This can be applied by hand, but when quantities of sheets have to be done, it is advantageous to use an offset roller-oiling machine with felt oiling-rollers. Periodic turning over of sheets to examine the underside is desirable, to check the adequacy of oiling and freedom from machine scratches.

5. HEAT-TREATMENT OF STRONG ALUMINIUM ALLOY COILED STRIP

Although processes have been proposed for the solution-treatment of strip in the flat condition in a single layer, between unwinding and rewinding reels, and one such installation has been described by Lamourdedieu,⁹ heat-treatment of strip in coil form can at present be regarded as the standard method.

It is not practicable to solution-treat a solid-wound coil, since not only would heating be slow and non-uniform, but quenching would be likewise, and water would penetrate irregularly between the close laps. This would be detrimental to the strip and possibly dangerous. It is therefore necessary to space the laps of a coil to permit the passage of the heating medium and of the quench water. In regard to the heating equipment, it has been found less satisfactory to heat coils in air-circulation furnaces than in salt-baths, owing to the slowness of heating, and incomplete and non-uniform attainment of temperature by coils in the former.

The first step in the heat-treatment process for coils is the rewinding of the as-rolled coil to space the laps. The spacing may be done in a number of ways. An early method was to set the coil on one of its flat faces, in a restraining box, and insert manually bent aluminium "hairpin" wires of about $\frac{1}{4}$ in. dia. at sufficient intervals to hold the laps reasonably apart. The coil was then rebound and lifted out to the heat-treatment frame. These hairpins were liable to cause scratches, however.

Another method consists in rewinding with the insertion along the edges of long lengths of corrugated strip, or open-coiled wire, or some such suitable open-spacing material in long lengths. If the spacing is excessive, the heat-treatment efficiency is in no way impaired, but the length of strip in the heat-treated coil may be much reduced.

A present-day standard method of spacing is by "dimpling". This consists in passing the strip through a set of dimpling rollers during rewinding. These dimpling rollers consist of a pair of narrow-faced rollers, 2 or 3 in. wide, mounted on driven arbors, geared together, one roller having holes around its periphery at predetermined spacing, and the mating roller having hemispherical-ended inserted punches to correspond with the mating holes. Holes and punches are about $\frac{1}{2}$ in. in dia. If the dimples are located too far apart, they do not provide adequate spacing for thin strip, which will then be pulled into contact between them. If too close, and regularly spaced, the dimples will frequently coincide on adjacent laps, permitting too many inter-lap contacts and inadequacy of spacing. To minimize the interlap contact, the pitch of dimples in a single row can be made irregular, though no intervals must be too wide; alternatively, 2 or 3 separate rows of dimples can be used, each row about $\frac{1}{2}$ in. apart, and with the dimples in zig-zag or other pattern. This gives a good reduction of coincidences and fairly even spacing, but

involves the scrapping of additional metal in the width, which increases the cost. In spacing by dimpling, a uniform distance between laps of $\frac{3}{32}$ – $\frac{1}{8}$ in. should be the aim, the dimpling punches being adjusted accordingly. This is an economical method, and good lengths of strip can be wound in coil; it is suitable for thicknesses up to 0.080 in.

The spaced coil must be wound true, with the ends flush, and be tightly bound. For economy it should be as large in diameter as will readily go into the salt-bath. Coils of thin strip, 0.028 in. and thinner, can with advantage be reinforced by an inner layer of thicker material. Coils are necessarily wound with their axes horizontal, and must be up-ended for resting on the sills of a furnace frame. This operation, as well as the reverse operation later on, must be carried out with care, or scratches will be made.

For salt-bath heat-treatment, the same type of bath is used as for sheets, the spaced coils being rested with the axis vertical on the floor of a steel frame; the floor is suitably composed of light transverse mild-steel angles, welded between longitudinal side frames.

The solution-treatment process in the salt-bath is similar to that for sheets described earlier, except that a longer time of immersion may be necessary.

6. SLITTING, FLATTENING, OILING, AND MARKING OF HEAT-TREATED COILED STRIP

After solution-treatment, the spaced coils are well drained, turned down-end, and mounted for unwinding in a roller-coil box, or preferably on a cone decoiler. The strip is then unwound and run through a slitter to cut out the dimpled band or bands, and to give the required width. It can then be run through a backed-up roller-leveller to remove the distortions of heat-treatment and produce a flat strip. At this stage the strip can be conveniently inspected, and then, if it conforms to one of the solution-treated-only specifications, it is marked on one side by means of a marking machine, as described for sheet, oiled similarly, and rewound on a reel or in an upcoiler for despatch. If a very high degree of flatness is required on thin strip, the strip may be cut into suitable lengths for stretching on a long-strip stretching machine. Machines suitable for stretching 50- and 150-ft. lengths are known or reported to be in use. The stretched strip is recoiled by hand or otherwise and rewound on the coiling machines, with marking and oiling if necessary.

It is quite feasible for all the above flattening processes, except stretching, to be carried out on one machine, combining the requisite number of different units. For the final rewind, a collapsing-type reel with suitable jacking-off trolley is convenient.

It must be ensured that slitting gives a good edge and removes the dimples completely, that flattening is adequate, and scratches are avoided. Therefore, all contacting surfaces must be faced with plastic material, cloth, or paper, and be dust-free.

Inspection takes place at the machine while the

strip is running through. If the rewind reel winds up from below, both sides of the strip can be viewed at this point.

7. PRECIPITATION-TREATMENT OF COILS

This is carried out when required, on the solution-treated, slit, flattened, and rewound coil as above, but, of course, before marking and coiling. It is of advantage, in order to avoid scratches, to interwind the coil with tissue paper before the precipitation process. After precipitation-treatment, the coil is unwound (the charred paper being removed), inspected, marked, oiled, and rewound as above.

IV.—EXTRUDED AND DRAWN PRODUCTS

In what follows it is assumed that the extrusion conditions themselves have been satisfactory in respect of quality of the product and, therefore, in the main, only factors affecting the quality in subsequent operations will be dealt with. The principal qualities to be controlled are :

- (i) Mechanical and physical properties.
- (ii) Dimensions.
- (iii) Straightness and squareness of section in relation to length.
- (iv) Truth of section profile.
- (v) In the case of tubes and hollow sections, minimum of eccentricity and ovality.
- (vi) Good surface quality in respect of colour and freedom from stains and surface damage, such as tears, &c.

1. NON-HEAT-TREATED EXTRUDED PRODUCTS

Practically speaking, processing subsequent to extrusion itself has a negligible effect on the mechanical and physical properties of the metal, although a slight improvement of the mechanical properties results from the cold work produced by stretching. Likewise, dimensional tolerances other than length are not affected by subsequent processing, apart from the slight reduction in area brought about by stretching, for which due allowance must be made in designing the extrusion die.

It is in regard to (iii) above, namely straightness and squareness of section in relation to length, that processing subsequent to extrusion can be most effective. In the case of unsymmetrically disposed or proportioned sections, there is the tendency, unless the extrusion die is suitably designed, for different parts of the section to extrude at different linear speeds, resulting in bow and/or twist of the section. It is in preventing such defects that the skill of the extrusion-die maker is apparent. These qualities are also affected by the differential rate of cooling of an unsymmetrical section. Finally, since the hot section is relatively soft, it can suffer distortion as it leaves

the die, although this can be minimized by careful leading out. However, practically all extruded sections require subsequent straightening or de-twisting or both.

There are a number of ways of effecting this, any of which can be used according to the section, namely :

- (a) Stretching and/or de-twisting.
- (b) Bending.
- (c) Roller-straightening.
- (d) Hand-straightening by a variety of means.
- (e) Reeling.

In regard to (a), although for very light sections stretching can be carried out by hand, using a ratchet-lever mechanism, practically all stretching is done on hydraulic machines ranging in capacity from 5 to 800 tons. In stretching, the metal must be loaded just beyond its proof stress.

A section often emerges twisted and, in the case of the lighter sections, this can generally be rectified by hand or with the aid of a hand tool during stretching. In the case of larger sections, twist is not normally troublesome, as it can be avoided to a large extent by good leading out from the press, if necessary under tension. However, when present, twist can be removed either during stretching by the use of a de-twisting head, or by a separate operation. Where a section is twisted in different directions at different parts of its length, a travelling de-twisting head is used.

Some very large rods or bar sections are more conveniently straightened by the use of a bending press. In this the bar is supported at two points and a ram is brought down on to it at an intermediate position to effect straightening. Presses for this duty range in capacity from 20 to 100 tons.

Some sections, particularly unsymmetrical thin-walled ones, do not respond to stretching, i.e. this process may cause deformation of the section, and in such cases the only satisfactory mechanical means of correcting for straightness and squareness is to use a roller-straightening machine—method (c). The section is passed through sets of rollers disposed so as to distort the section uniformly in the early rolls and to take out the distortion in the later rolls.

There are many intricate sections which do not respond to this or any other method of mechanical straightening. In their case, it is necessary to resort to method (d), i.e. hand-straightening, a procedure that calls for considerable skill and ingenuity on the part of the operator. Essential tools for the purpose are a surface table, fixed floor-stands with adjustable anvils, straight edges and set squares, &c. The operator has to tap the section into shape, using wooden mallets and formers and suitable clamps.

Method (e), reeling, can be used only for round rods and tubes. The machine generally consists of two driven rollers on one side with axes roughly at right angles to three or five adjustable backing-up rollers on the other side, so that the work can be passed through with a rotatory motion. Adjustment of the idle rollers demands some practice if straightening is

to be effected in one pass. In certain cases where a good finish is required, reeling is not used because of the spiral marks left by the rollers, although this, too, can be almost eliminated by skill and by increasing the number of passes.

In regard to requirement (iv), i.e. truth of the section profile, it is often very difficult, or even impossible, to ensure that the several members of a section are in the correct angular relationship to each other in the as-extruded condition. Hand correction is usually adopted, but correction by suitable machines with specially designed rollers is much cheaper, and is justified except in the case of complicated sections.

With reference to requirement (v), the maintenance of a good surface, a great deal of damage can be caused as the section runs out from the extrusion press, i.e. while it is still hot. The rollers over which it runs should be kept clean and free-running. Any sharp edges will indent the metal and any loose pieces of metal are liable to be pressed into it. A common practice in North America is to line the sides and bottom of the run-out table or trough with graphite blocks. Care should be taken in handling at all stages, particularly when hot, and suitable racks and tables must be provided for cooling, storage, and sawing.

Cutting to length is sometimes done by sawing without any special arrangements, the section being merely pushed up against a stop and traversed by hand across the blade, but to obtain a perfectly square cut, the work must be clamped and either traversed through the blade on a movable table or held rigid and cut with a movable downcutting or pull-across blade. The main quality requirement in sawing to length is to give a good clean edge as free as possible from burr, and to ensure that the sawn pieces do not pick up loose swarf. It is better to work with no set on the teeth and to use thin machine oil as a lubricant.

The inspection of the final product, apart from mechanical testing, depends very much on the particular end-use, the customer's requirements, and the alloy. In practically all cases the back ends of extrusions are those which are selected for a detailed examination, for it is at the back of extrusions that the lowest properties are usually obtained. It is also in this region that extrusion defects are found. In the case of sections subject to approval by A.I.D. or an equivalent inspecting authority, samples are taken from the back ends and etched, and, in the case of multi-hole extrusion, samples must be representative of each hole. Before etching the samples are machined, and after etching they are examined for coarse grain, coring, &c. A further test frequently carried out is a fracture test at the back end of a rod or bar section. Though not so positive as the etch test, a fracture test does, in general, show up any signs of coring. In the case of, say, an aluminium-5% magnesium alloy section, a bend test with $R = \frac{1}{2}T$ is carried out on the mechanical test samples to ensure freedom from excessive primary intermetallic constituent.

2. NON-HEAT-TREATED EXTRUDED AND DRAWN PRODUCTS—TUBES AND SECTIONS

The process of drawing has several effects:

(a) Without reducing the sectional area of the piece, it can correct the profile or bring it to the required shape. Such a correction generally raises the mechanical properties slightly.

(b) It can be used for a final sizing operation on rod or bar in order to meet closer tolerances than can be obtained by extrusion only. Used in this way, drawing gives, of course, a small reduction in sectional area, and the mechanical properties are noticeably increased.

(c) In the case of tubes, a significant reduction in area is brought about in the course of drawing, so that, depending on the reduction effected, a particular set of mechanical properties can be obtained. Further, drawing corrects any ovality but does not reduce the percentage eccentricity present in the extruded tube shell.

In regard to (a) and (b), certain sections cannot be produced by extrusion only and have to be drawn to the required shape or size. Examples are: (i) sections produced from strip which are too thin to be extruded in the purity or alloy required; (ii) sections which, although not too difficult to extrude, necessitate the use of an inherently weak extrusion die, e.g. split tubes with a narrow gap; (iii) sections which give great difficulty with regard to shape and must be corrected on a drawbench; and (iv) certain rods, bus-bar, and other sections required to very close tolerances. Sections in category (i) are drawn from rolled strip in coil, those in category (iv) are produced by extrusion and drawing, and the other two can be produced either way. The required shape or size can normally be obtained in one pass, but for very complicated sections two passes are sometimes given.

The drawing process is mainly used for (c), i.e. to effect a significant reduction in sectional area of tubes. There are three methods of reducing the sectional area: (a) mandrel-drawing, (b) plug-drawing, and (c) sinking. There is a method, different entirely from drawing, which is widely used for effecting a substantial reduction in the area of tubes, namely by tube-reducing machines, in which the tube shell is worked down to the desired finished size by roller-type dies which are given a reciprocating rotary motion, the tube being fed slowly forward through the dies supported on a mandrel, and turned at appropriate intervals. There is a lot to commend this method in the case of the harder alloys on the score of much heavier reductions per pass compared with drawing; less scrap, the use of thicker and, therefore, cheaper extruded shell; and more even wall thickness.

Drawing by methods (a)–(c) is usually carried out on a drawbench, but it can also be carried out by pulling the tube through the die and winding it on to a drum, i.e. by means of a "bull block"; this is referred to in more detail later (p. 215).

The difference between mandrel-drawing and plug-

drawing is that, in the former case, the mandrel which supports the tube is pulled through the die and draws the tube with it, whereas with plug drawing the plug occupies a fixed position in the die orifice and the tube is pulled through the annular space between the plug and the die. In sinking, neither a mandrel nor a plug is used.

In mandrel-drawing, one end of the tube shell is first tapered by holding the shell vertically and thrusting one end repeatedly into a die of suitable shape. The tube shell is then threaded over the mandrel, one end of which protrudes through the tapered end of the tube shell. This mandrel end and the tapered part of the tube are pushed through the drawbench die, the front end of the mandrel having an eye or lug which is engaged with the drawbench dog, and the mandrel is then pulled forward through the die, bringing the tube with it. The friction forces between the mandrel and die tend to balance out, and since the opposite effect occurs with plug drawing, a much higher reduction in area per pass can be taken with the former method, although it is slower.

Provided that a mandrel is available, mandrel-drawing is used for tubes measuring about 3 in.-dia. and over $\times \frac{1}{8}$ in. wall and thicker, except when especially close tolerances on thickness or bore are required. In those cases and when no mandrel is available, plug-drawing is used. A disadvantage of mandrel-drawing is that the resultant tube has a tapered bore owing to the fact that the mandrel, which is up to 20 ft. long, has to have a taper of approximately $\frac{1}{32}$ in. on 20 ft. in order to enable the tubes to be readily stripped off after drawing. However, a much straighter tube can be obtained. It will be appreciated that the operative surface of a small plug can be more readily maintained in a good condition than can a long mandrel, and, in consequence, that plug-drawn tubes usually have a better inside surface than mandrel-drawn tubes. To minimize the reproduction of mandrel defects on the bore of the tube, the mandrel, of course, must be well lubricated before the tube shell is threaded on to it, and mandrels must be frequently hand-polished with emery paper to keep them in the best possible condition. It is common practice before mandrel-drawing to soda-dip all mandrel-extruded tube shells and certain shells extruded through porthole-type dies. This is partly to give them a good clean bore by removing any graphite lubricant remaining from the extrusion process and partly to aid lubrication. A soda-dipped tube shell can always be mandrel-drawn more easily than a non-dipped shell and is very much less liable to tear.

With plug-drawing the reductions attainable per pass vary considerably, depending on the size, alloy, and temper of the tube concerned; thus, on an annealed small-diameter tube in pure aluminium, a reduction of 40% may be obtained, whereas only 10% would be possible on a thick-gauge aluminium-magnesium alloy tube. In the case of a drawbench, the plug is secured to the end of a long rod, the tube shell being threaded over this rod, the end of the tube

next to the die having first been pointed in a swaging machine. This swaged end is put into the die and pulled through by the drawbench dog, the plug taking up a fixed position in relation to the die. The tube shells, before drawing, are sometimes oiled by immersion in a large tank, and during drawing, after the first pass, the plugs and outsides of the tubes are oiled by hand. With more modern drawbenches, oil is continuously pumped into the bore of the tube shell and over its outer surface just before it enters the die. It is necessary, for the sake of avoiding surface tearing, both internal and external, to ensure that the oil is in a clean condition and is copiously applied.

The main requirement in regard to plug and die profiles is to have a minimum of parallel bearing surface of the correct diameter with gradually flared entry and exit approaches. It is most important to keep the tools in a reasonably well-polished condition, so that die and plug marks are avoided, and in cases of bad metal pick-up, polishing after every three or four tubes may be necessary. It is also important to apply liberal quantities of oil to the die and plug, the oil best suited to the purpose being a very viscous, compounded mineral oil specially designed for wire and tube drawing.

Plugs and dies are generally made of 0.9% carbon-1.25% tungsten-0.5% chromium-1.0% manganese steel, heat-treated to about 600 Brinell hardness number. Where the size of the orders warrants it, dies fitted with tungsten-carbide inserts are used, as these maintain the required size, whereas steel dies gradually wear bigger. Tungsten-carbide plugs are not used, owing to the greater risk of breakage.

Plug-drawing is possible down to, say, $\frac{3}{8}$ in. internal diameter of tube; below this, it is customary to carry out the final reduction in producing small-diameter tubes by sinking. This process results in a decrease in external diameter and in the area of the tube. Generally speaking the wall thickness is either unchanged or slightly increased, but by the use of different die shapes a certain amount of control of wall thickness can, if necessary, be exercised. If sinking is carried too far, the bore of the tube acquires a puckered or fluted profile. The outer surface of sunk tubes is more liable to be pitted than in the case of plug-drawn tubes, because the whole of the drawing load through the die is taken on the outside surface, whereas in the case of plug-drawing, for the same reduction in area, the frictional force is distributed over outer and inner surfaces.

Bull-block drawing is particularly suitable and advantageous in the case of pure aluminium and the softer alloys in tube diameters up to, say, $\frac{3}{4}$ in. For the harder alloys of the Mg_2Si type, it is by no means as advantageous as for pure metal and the softer alloys, because usually only one pass is possible with the Mg_2Si -type alloy, fractures of the drawn tube being liable to occur on the second pass at the plug mark as it bends on to the drum. With still harder alloys, such as those containing $2\frac{1}{4}\%$ and more magnesium, only comparatively short lengths are

extruded, so that even if bull-block drawing were possible, it would not have much advantage over ordinary drawbench practice.

Only when coiled tube is required, is it possible to finish on the bull block. Normally, to obtain straight lengths, a final sink from coil on a drawbench is given. This procedure, incidentally, also gives a less oval tube than can be obtained on the bull block. It is necessary to use two dies simultaneously mounted one behind the other, the first die giving a sinking pass and the second die, in conjunction with a plug, giving a plug-drawn pass. The aim should be to sink the tube in the first die so that the bore of the tube is some 0.008-0.012 in. larger than the ball of the plug used in the second die. In setting up the machine, a sufficient quantity of oil to draw the coil is first injected into the tube and then the plug is inserted some 2-3 ft. into the same end, which is then pointed to allow the end to be passed through the two dies and gripped by the dogs. The tube is then inched through and when the plug has advanced into position in the second die, the block is accelerated to its maximum speed, the plug staying fixed in position until the coil is drawn. The object of the ball is to locate the plug correctly in relation to the die. Fig. 1 shows the plug profile which has been found most suitable.

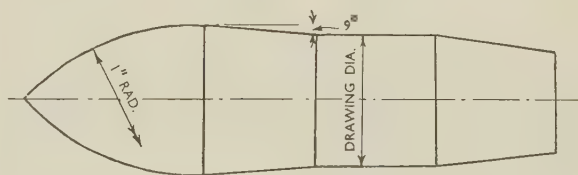


FIG. 1.—Enlarged Profile of Plug Used for Bull-Block Drawing. (The drawing diameter is equivalent to the required bore of tube.)

For bull-block drawing the same dies can be used as for drawbench drawing, and the same steel can be used for the bull-block plug as for the drawbench plug. Lubrication of the bore has been mentioned earlier; lubrication of the outer surface is effected by automatic spraying of the oil at the point of entry to the dies. Bull-block-drawn tubes usually have brighter bores than drawbench-drawn tubes, but the outer surfaces are more pitted.

Pitted-surface defects on drawn tubes can be very troublesome whatever the method of drawing, in spite of every precaution being taken in regard to lubrication and cleanliness of the die surface. The defect is more severe with thinner- than thicker-walled tubing and on strong alloys. It takes the form of minute pits, sometimes small transverse cracks, and is attributed to local breakdown of lubrication in the die. The most effective means of preventing or minimizing it is to ensure absolute cleanliness of the tube shell, with freedom from scratches, and to use a high "draw : sink ratio" procedure. With this, two dies are used simultaneously for the first pass, a heavy sink being taken through the first die and a plug pass through the second. After the first pass, all sub-

sequent ones (unless final sinking is necessary) are plug-drawn so as to reduce the bore on each pass by about 0.012 in. The practice, while it nearly always gives a bright tube with little pitting, entails the use of non-standard sizes of plugs, and a slightly decreased drawing rate.

The following are typical examples of drafting schedules :

(a) *Mandrel-Drawing*

(i) For pure aluminium in hard temper, a $4\frac{1}{2} \times 4$ in. shell would be drawn to $4 \times 3\frac{3}{4}$ in., giving a 53.8% reduction.

(ii) For an aluminium-3½% magnesium alloy tube in ½-hard temper, a $3\frac{7}{8} \times 3\frac{1}{4}$ in. shell would be drawn to $3\frac{1}{2} \times 3$ in., giving a 26.9% reduction.

(b) *Plug-Drawing*

(i) A 1×0.0225 in. cycle-pump tube in an aluminium-Mg₂Si alloy would be given a 71-74% reduction without annealing in accordance with the following drafting schedule :

Die, in.	Plug, in.	Wall, in.	Reduction, %
$1\frac{1}{4}$...	0.072 max.	...
1.122	1.010	0.056	29.3
1.086	0.996	0.046	20.0
1.054	0.982	0.036	23.2
1.024	0.968	0.028	23.7
1	0.955	0.0225	21.2

(ii) A $\frac{3}{16}$ -in.-dia. \times 0.022 in. thick tube in an aluminium-2½% magnesium alloy in soft temper would be drawn in accordance with the following schedule, which illustrates the use of the sinking process in the last pass :

Die, in.	Plug, in.	Wall, in.	Reduction, %
$\frac{7}{8}$...	0.064	Levelling pass
$\frac{3}{4}$	0.628	0.061	16.5
$\frac{11}{16}$	0.589	0.049	25.6
$\frac{1}{2}$	0.545	0.040	25.8
$\frac{9}{16}$	0.496	0.033	25.0
$\frac{5}{8}$	0.444	0.028	24.5
$\frac{3}{4}$	0.422	0.022	25.5
$\frac{7}{8}$	0.399	0.019	18.8
Process anneal			
$\frac{11}{16}$	sink	0.020	18.7
$\frac{1}{2}$	"	0.021	25.8
$\frac{9}{16}$	"	0.022	18.8

(c) *Bull-Block Drawing*

A pure-aluminium tube, $\frac{5}{8}$ in. dia. \times 0.064 in. thick in hard temper, would be given a 52% reduction in two passes on the bull block and one on a light drawbench as follows :

Die, in.	Plug Ball Dia., in.	Plug Drawing Dia., in.	Wall, in.	Reduction, %
$\frac{7}{8}$	0.092/0.100	...
$\frac{3}{4}$	0.632	0.606	0.073	36.3
0.652	0.596	0.530	0.062	26.8
Sink to $\frac{5}{8}$ in. outside-dia. straight lengths from coil on light drawbench				
$\frac{5}{8}$	sink	...	0.064	2.5

Practically all drawn tubes, rods, and bars, and some sections, require straightening after drawing and

two methods are available, hand or hydraulic stretching, or "reeling". Reeling is the cheaper method and is effective, but it produces spiral marks along the tube or rod. Reeling can also be used for thin-walled or soft tubes, but the process may cause collapse if extreme care is not taken. Mandrel-drawn tubes do not require subsequent straightening.

The process of drawing requires copious lubrication, and before packing and despatch, it is necessary to remove residual oil by a trichlorethylene-vapour degreasing process.

Inspection of tubes involves a check on outside and inside diameters, wall thickness, and degree of ovality and eccentricity, to ensure that the tubes conform to the relevant British Standard, industry-sponsored, or customer-specified tolerances. In addition, the tubes are inspected for straightness and surface condition, both inside and outside, although the former, of course, is a matter of some difficulty and becomes impracticable in the smallest sizes. Standards in regard to surface quality, straightness, and, in some cases, tolerances on dimensions are, apart from what may be laid down in the official specifications, largely a matter of experience of customer's requirements. It is also necessary to carry out several special tests in addition to normal mechanical testing; for example, tubes which have emanated from port-hole-type extrusion-dies are not only drift-tested at the ends of each extrusion, but are checked for soundness throughout their length by an electronic tube-testing instrument. Tubes are also hydraulically tested. They are plugged at each end and subjected to hydraulic pressure varying according to diameter and wall thickness and alloy from 200 to 4000 lb./in.².

3. HEAT-TREATED EXTRUDED AND EXTRUDED AND DRAWN PRODUCTS

Solution-treatment of extruded sections can be carried out in two ways :

(a) By quenching the section on emergence from the extrusion press, relying on the section leaving the press, immediately before quenching, being at the required solution-treatment temperature.

(b) By separate solution-treatment and quenching in heat-treatment plant designed for the purpose.

Method (a) is to be preferred to method (b) on the score of economy, but is suitable only for medium-strength alloys; press-quenched sections usually suffer less distortion than separately furnace-treated sections. However, there is a limit to the size of section which can be satisfactorily press-quenched. With the larger sections, quenching on extrusion becomes ineffective, since the heat cannot be dissipated sufficiently quickly in the quenching box without reducing the extrusion speed to such an extent that the section temperature drops to below that required. The limiting size for press-quenching varies considerably with the alloy and the type of section; as an example, simple shapes such as channels in H10 alloy up to about 6 in.² can be press-quenched

effectively. It is important that the billet temperature be kept as close as possible to the solidus temperature, so as to ensure that throughout the extrusion the temperature of emergence is higher than the minimum for solution-treatment. Only the billet temperature is actually measured, however, and this is controlled within a 20° C. range, as near as practicable to the solidus temperature. For example, structural sections in H10 alloy extruded with an emerging temperature of 520°–540° C. require a preheating temperature up to 40° C. higher.

In regard to method (b), i.e. solution-treatment in a separate furnace, it is easier than with press-quenching to ensure that the required solution-treatment temperature is observed. With the aluminium–Mg₂Si alloys, quite a wide latitude in temperature, e.g. 520°–560° C., is permissible, but in the case of the stronger alloys, for example those to specifications B.S. L.64 and L.65, as used for aircraft construction, a closer tolerance on temperature has to be observed, namely $\pm 5^\circ$ C.

With horizontal batch-type furnaces, a charge of sections weighing anything from 10 cwt. to 1 ton is carried in a steel basket in a cylinder-shaped furnace through which air is circulated along the length of the chamber at about 40 ft./sec. With a heating chamber measuring, say, 30 ft. long \times 3 ft. wide \times 2 ft. deep, the charge takes approximately 30 min. to attain the required temperature; for smaller sections the charge is soaked for about 1 hr. at this temperature, whereas for larger sections—for example equivalent to 4 in.-dia. rods and over—soaking times up to 6 hr. may be necessary. The temperature of the furnace atmosphere is used for control purposes, and in view of the high air speed and the time of treatment, the charge temperature soon reaches the air temperature, which is checked and recorded by three separate pyrometers and controlled by a fourth. The charge temperature itself can be checked if so desired, but normally this is unnecessary.

A disadvantage of the batch-type furnace is that the charge leaves the furnace horizontally at the end of the heating cycle and enters the quench tank at a slight angle to the horizontal. In consequence, the front ends and the under-sides of the sections are the first to be quenched, and considerable quenching distortion can thereby result, particularly with relatively small sections and tubes. For this reason there has been a growing tendency to use vertical-type heat-treatment furnaces. Even with these some distortion occurs, and as subsequent correction by stretching, &c., is needed in any case, it is doubtful whether the use of the vertical-type furnace is entirely justified, having in mind the complications in handling and installation involved. A claim made for vertical-type furnaces is that the rapid quench ensures compliance with the specified properties and less liability to stress-corrosion. Another type of furnace which, it is understood, has proved effective is a form of continuous horizontal furnace in which each length of section travels sideways across the width of the

furnace; during this passage the sections attain, and are soaked at, the solution-treatment temperature, and are then discharged singly, one after the other, through a rapid quenching zone. Something like press-quenching is obtained in this way, and it is possible to apply the quench uniformly throughout the length and round the periphery of the section. It is understood that distortion with this method is very small, but that subsequent straightening is still required.

Salt-baths are also used for the solution-treatment of extruded sections, but they seem to have no particular advantage as distortion resulting from the horizontal quenching of a batch of sections is just as great as with quenching from a batch-type air furnace, and there is the disadvantage of the removal and loss of salt. More rapid heating, of course, is obtained with a salt-bath than with an air-flow furnace, but this does not appear to be of importance in the case of extruded sections which are unclad and in which, therefore, no problem of diffusion arises.

The straightening and rectification of solution-treated sections and tubes, necessitated by the quenching distortion, are more difficult than in the case of non-heat-treated material. The straightening and rectification processes are preferably carried out as soon as possible after solution-treatment, i.e. while the material is still soft and before it has shown a noticeable improvement in properties as a result of age-hardening. However, provided that full use is made of stretching, de-twisting, press-bending, and the various methods of hand-straightening and profile correction, a satisfactory product can be obtained, but to carry out these processes on heat-treated sections is inevitably expensive. A judicious arrangement of the charge in the solution-treatment furnace helps to minimize the extent of subsequent processing; for example, channels should be laid in the carrying basket so as to be supported on the web with the flanges standing vertical, and angles should be laid with one leg horizontal. Sections should, if possible, be kept well separated from each other and, at intervals throughout their length, should be securely tied by wire to the framework of the carrier basket if they are relatively light. In the case of tubes, however, despite such precautions, it is always necessary to give a light pass or sink (about 15% reduction in area) after quenching and stretching.

The precipitation-treatment or artificial ageing of extruded sections and extruded and drawn tubes is carried out in horizontal furnaces similar to those described above for the solution-treatment in batch, although, of course, the temperatures are much lower. For example, sections of the H10 type receive a precipitation-treatment of 6 hr. at 175° C. In the case of H10 tubes the precipitation time is reduced to 2 hr. in view of the cold work that the tubes have had between solution- and precipitation-treatment.

Usually, in the case of heat-treated sections and tubes, the material is required to be supplied to official specifications, and may also be subject to

inspection by approved inspectorates. There is, of course, the necessity for accurate identification of the finished material, not only with the original cast billet, but with the heat-treatment batches, and it is the duty of the approved inspectorate to see that a proper identification system is in operation.

V.—INSPECTION AND TESTING

For some of the groups of products dealt with, reference has already been made to those inspection features which are peculiar to them. There are, however, general considerations in regard to all products. In several rolling mills and extrusion plants the responsibilities for inspection and testing are organized as follows:

(a) A large amount of the material produced is required to comply with one or other of a wide variety of commercial standards and specifications. None of these standards or specifications requires that the material shall be subject to acceptance by some inspecting authority. For most of the material produced, inspection is carried out by an Inspection Department responsible to the management only and not to any outside body. This department is responsible for ensuring that the products sent out of the factory comply with standards laid down by the management in respect of surface quality, flatness, &c., appropriate to the end-use and type of product. These standards are flexible and vary widely between one product and another and between one end-use and another. The closest possible liaison, therefore, has to be maintained between the producer and the customers.

(b) For all other products, the inspection standards are controlled by an outside authority such as the Aeronautical Inspection Directorate or the Chief Inspector of Armaments. Although these authorities may, on occasion, carry out inspection themselves, it is customary for them to delegate the actual inspection to what is termed an "approved inspectorate" in the producer's organization. This approved inspectorate is entirely different from, and separated from, the Inspection Department referred to in (a). The usual practice is to have at each factory a Chief Inspector of the approved inspectorate, who is responsible not to the management of the factory, but directly to the outside authority. Working directly under the Chief Inspector are laboratory testing personnel and inspectors, the latter being concerned with surface quality, flatness, dimensions, &c. Each inspector has his or her own personal stamp which is applied to the material approved. These inspectors are responsible, in regard to the standards they observe and the quality of their work, only to the Chief Inspector. They are employees of the producer, but the management has no control over the standards they observe. Naturally the Chief Inspector and his staff maintain close liaison with the management, but it can be said that the approved inspectorate is entirely

independent of the factory management and is an impartial inspecting organization within the factory.

(c) For all products, whether of the commercial variety or those subject to outside inspecting authority, mechanical and physical testing, as well as analysis, is carried out in the laboratory associated with each factory. This laboratory, in regard to its methods of testing and analysis, is usually entirely independent of the management. The acceptance or rejection of the material on the test results obtained depends, in the first instance, on the class of material. If it is subject to an official specification, failure to meet the requirements of that specification results in rejection. If, however, the material is subject, not to an official specification, but only to the producer's own specification, material on the borderline of rejection may, on occasion, be accepted if the circumstances, particularly the end-use for which the material is required, warrant it.

Compared with practice in the engineering and allied industries, there is little process inspection in light-alloy fabrication. By "process inspection" is meant the inspection of the product at intermediate stages of its manufacture, and there is little scope for such inspection because the product is changing its form continually. Further, inspection is a relatively slow process and to associate it with a production process would slow up the latter. However, when process inspection is convenient, it is advisable for it to be done so as to ensure that later expensive processes are not carried out on faulty material.

The following are some examples of process inspection that have been found useful. To ensure that sound billets only are sent to the extrusion presses, the cast billets are subjected to an examination by supersonic crack-testing equipment. A similar treatment is sometimes carried out with rolling slabs. Hot-rolled slab or plate may be similarly tested; defective material, usually in the form of laminated zones at the ends of the hot-rolled slab, is cut out at this stage. In cutting up coiled strip into flat sheets, the operators themselves act as inspectors and discard over-gauge and badly off-shape sheets. Process inspection can profitably be carried out also immediately following solution-treatment, particularly in respect of such defects as blister and bad abrasion marks which would clearly result in final rejection after further processing.

Inspection of most light-alloy products, however, is mainly confined to the final inspection immediately before packing and despatch. This inspection is carried out usually in an inspection section of the packing and despatch department, and, with a suitable layout, it is possible for accepted material to be packed simultaneously with inspection. This, of course, minimizes the risk of defects occurring between inspection and packing, and faulty material being sent undetected to the customer.

A very large variety of inspection standards are observed in respect of surface quality and flatness. Thickness measurements are carried out on all, or on a

fraction, of a batch of material undergoing inspection, depending on the specification or standard to be observed. Surface measurements, length, width, diameter, &c., are also checked to the same extent, squareness to sides of flat rectangular sheets being checked on a suitable number of sheets by measuring the two diagonals. If these are equal, then a true rectangle is deemed to have been produced.

A control feature of considerable importance is the maintenance of the identity of the metal throughout processing until inspection and despatch. This identity is given in the form of stamped markings on the pieces, or, when such a marking is likely to disappear in the course of processing, e.g. rolling, then stamped tags or labels are attached to the piece or to a batch of pieces. The identification which it is important to maintain is the cast number of the original slab or billet and the identity of the heat-treatment batch. It is one of the functions of the approved inspectorate already mentioned to ensure that an adequate system of metal identification is practised and strictly adhered to. It is, of course, essential that the same identity marks should be given to *samples* taken from work in process, or from a batch of material at inspection, as is given to the bulk material itself.

In addition to the physical marking of work in process and at inspection, and of samples taken therefrom, it is most important to ensure that the specified production procedures, as laid down on mill cards, have been followed. These precautions may seem to be elementary, but, with the considerable variety of conditions in respect of alloys, tempers, heat-treatments, &c., it is possible for occasional lapses to occur unless constant supervision and scrutiny of identification and sampling are maintained. This can be ensured not only by patrol inspectors forming part of the approved inspectorate, with special reference to the products for which they are responsible, but also by a system of quality-control inspectors whose job it is not only to watch for and correct any errors in procedure and departures from the production conditions laid down, but also to ensure that the intricate system of identification and sampling is maintained.

The rate of sampling for mechanical and physical testing depends on what is laid down in the relevant specifications, and when sampling rates are not specifically laid down, they are determined by experience of ultimate performance in the end-use of the material. It has been shown by Whyte¹⁰ that optimum sampling rates can be determined statistically. To assist in statistical control of quality, very complete documentation and recording systems covering all processing conditions and inspection and testing results, must be maintained. It is only by having the maximum information and by making a thorough statistical examination of it, that the fullest use can be made of the final check on quality which is made at inspection. The function of inspection is not only to accept good material and

reject bad, but to provide the management with data by means of which the causes of bad quality can be traced and quality can be improved and properly controlled.

Mechanical tests are commonly carried out to determine the 0.1% proof stress, the ultimate tensile stress, the percentage elongation (or bend test), and hardness. Hardness testing is not regarded as a precision method of checking that the material satisfies the desired mechanical properties, but is mainly a means of ascertaining whether the material is in the required condition of temper or heat-treatment. In addition to mechanical testing, certain physical properties, such as grain-size and earing on materials intended for deep drawing, are also determined.

VI.—PACKING

A high proportion of the complaints made by customers arises from defects caused by faulty packing or damage in transit. The type of packing naturally depends on the product and on the end-use; if a customer has ordered a high-grade product, a superior form of packing is used. In other cases, where a high standard of product is not required, a simpler form of packing suffices. There are four main types of packing: (a) in completely closed cases, (b) in crates, (c) in packages protected top and bottom by boards or battens strapped together, and (d) in the case of some extruded sections, it is sufficient to bundle the pieces together and secure them by wire.

Completely closed cases are used to protect the metal from corrosion due to dampness, and from handling damage in transit. Flat sheets for export markets, panel-quality sheets for bus and coach building, sheets for the aircraft industry, circles for holloware, &c., should be packed in closed cases. Such material as lower-grade commercial flat sheets and corrugated sheets are packed in crates or top- and bottom-boarded packages as mentioned in (c). The bulk of material requires to be packed in cases or crates, and, in addition to the protection afforded by the timber, it is necessary to wrap the product in waterproof paper properly sealed at the joints to prevent the ingress of dust and water. It is also necessary to ensure that the contents are tightly packed in the cases or crates and cannot possibly move. It has been found that the slightest movement of sheets relative to each other when in transit in a case causes minute abrasion marks and may give rise to what is known as a "black spot" defect. To minimize this risk for some products, particularly the softer, thinner ones, and those intended for special end-uses, as in the aircraft industry, it is customary to interleave the sheets with tissue paper. For materials for aircraft construction, not only are sheets and coiled strip oiled before despatch, as already described, but extruded sections are also oiled, usually by immersion and then draining off the surplus oil.

The timber used for the cases must be dry. Empty cases returned from customers are often in a wet condition, and tests have shown that they can contain as much as 15% by weight of water. Clearly this water must be removed by drying before they are re-packed.

Before despatch from a factory, material may lie in the warehouse for some time, and to avoid the risk of corrosion it is advisable to exercise a reasonably close control on the temperature of the warehouse or despatch department. Unless this is fairly constant, there is a risk of differences arising between the atmospheric temperature in the warehouse and the temperature of the metal being stored, with resultant condensation on the metal. Cases must be very robustly constructed, particularly those used for the transport of large sheets. Such cases are often lifted by crane slings, and unless the case is very rigid, it may deflect under the load, and minute inter-sheet movement may occur, causing abrasion and black spot marks. Carelessness in nailing up the case can cause a lot of damage, not only because of the obvious possibility that nails may be driven into the contents, but because the latter, as they are withdrawn by the customer, may be damaged by protruding nail heads.

VII.—GENERAL QUALITY PRECAUTIONS

Finally, it is considered appropriate to mention certain factory conditions, methods of handling and transport, to which attention should be paid if a good-quality product is to be obtained. Light-alloy products, as is well known, are more susceptible to damage than harder metals, and in addition, the end-uses made of light alloys demand a higher surface quality than is often required from many other metals. In consequence, the light-alloy product must, throughout all stages of production, be handled with more care than other metals. For example, in the processing of flat sheets, particularly thin ones, it is customary to interleave the sheets by tissue paper or brown paper throughout all final processing from flattening onwards. Such interleaving may, in fact, be carried out at the various rolling stages when rolling is done in flat-sheet form. Operatives must be taught methods of handling the sheets in such a way as to ensure that the surface of one is not scratched by its neighbour, and that kinks and other damage are not caused. For example, in lifting sheets one after the other from a stack adjacent to a machine, it is usual for the sheet to be turned over in the course of transfer. It has been found by experience that, by combining turning with lifting and transfer, the sheet can be more readily handled without kinking and without scratching its neighbour. For special products,

clean soft gloves are worn by the operators, not only as a personal protection, but to avoid finger-marking the highly lustrous metal.

To obviate damage to the product, the transport equipment used for conveying it from one process to another must be robustly constructed, easy to manoeuvre, adequate for the duty, and its hard metal parts must be covered by protective material. The factory building, particularly the floors, must receive attention. It is a common complaint that defects which have been observed in light-alloy sheets have arisen because of dust picked up from the atmosphere in the factory. A lot of this dust arises from the floors and can be kept to a minimum by a proper system of floor cleaning, preferably by having floors of the non-dusting type, particularly along traffic-ways. There should, of course, be adequate space in a factory for the loads to be moved about without collision.

Continuous and adequate attention should be given to all production and quality-control instructions, particularly those relating to pyrometric equipment and methods, and the factory maintenance department should be alert to the necessity for keeping production plant in first-class condition, giving special attention to the protective materials used for machine beds, &c.

There is no doubt that, quite apart from clearly definable production conditions that must be observed to ensure a high quality of product, the main contribution to quality must come from the care and co-operation of the operatives. This calls for their proper training, particularly in the case of new recruits, and constant vigilance on the part of supervisors to ensure that the requisite precautions are observed.

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REFERENCES

1. F. King and A. N. Turner, *J. Inst. Metals*, 1953-54, **82**, (7), 291.
2. C. Smith and N. Swindells, *ibid.*, 323.
3. C. P. Paton, *ibid.*, 1951-52, **80**, 311.
4. R. T. Staples, *ibid.*, 323.
5. H. C. H. Carpenter and C. F. Elam, *ibid.*, 1921, **25**, 259.
6. F. King and A. N. Turner, *ibid.*, 1953-54, **82**, (7), 303.
7. F. King and A. N. Turner, *ibid.*, 292.
8. —, German Patent No. **244,544** (1909).
9. M. Lamourdedieu, *J. Inst. Metals*, 1951-52, **80**, 335.
10. M. Whyte, *ibid.*, 1953-54, **82**, (7), 334.

HEAT-TREATMENT AND FINISHING OPERATIONS IN 1591 THE PRODUCTION OF COPPER AND ALUMINIUM ROD AND WIRE *

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SYNOPSIS

In view of the importance attached to the surface quality of wire products, a broad review is first given of the factors which determine this feature. This is followed by a general consideration of those characteristics of copper which are of prime importance in annealing; the various types of commercial annealing processes, their principal features and limitations, are then discussed, mainly from the point of view of control of quality. The testing of copper wire is reviewed, with particular reference to springiness, in view of the importance of this property in certain industrial applications.

The paper also deals with annealing and heat-treatment operations as undertaken on aluminium and aluminium alloys in wire form. General observations on the inspection and packaging of wire are also included.

I.—INTRODUCTION

HEAT-TREATMENT and finishing operations for wire and rod products naturally vary with the characteristics of individual materials and, in addition, the dimensions and the particular purpose for which the product is required are of great importance, often necessitating considerable modifications in procedure. A review on a broad basis of the requirements for commercial heat-treatment would run the risk of giving an excessively simplified account of the subject, and hence it has been thought more useful to consider a few specific products and procedures in some detail.

This has been undertaken more particularly in the case of copper wire and shaped sections, which are used in large quantities, both annealed and hard-worked, for electrical purposes. Aluminium and aluminium alloy wire in the heat-treated condition is not in wide use, and there is less experience on which to draw, but attention has also been given to its processing. To a large extent, therefore, this paper is devoted to wire and rod materials and products manufactured for electrical requirements.

One point, to be stressed at the outset, is that procedure is determined by the overriding consideration that products should be manufactured in the most straightforward and economical manner, consistent with the attainment of a satisfactory standard of quality. The standards demanded depend on the particular use for which the product is required, and naturally they tend to vary with progress. The further processing operations carried out by users quite often call for special features in the products, so that the processes which are under the

control of the fabricator must be modified accordingly. Thus, to a large extent, the rod and wire industry might be said to be organized on the basis of manufacture of products in batches for a particular customer or section of the user industries. This remark applies particularly to surface condition, to which further attention will be given later.

II.—INFLUENCE OF EARLY PROCESSING OPERATIONS

Although it was first intended to restrict this paper to a consideration of annealing and finishing operations, it has been found necessary to take into account the preceding manufacturing processes, as many of these influence the properties of the final products. Briefly, the requirements to be met concern (1) surface condition, (2) mechanical properties, and (3) electrical conductivity, in descending order of importance, from the point of view of the precautions necessary in manufacture.

Surface condition is the feature which is most affected by the early processing operations, and with both copper and aluminium, careful attention must be given to: (1) choice of fabrication methods, (2) quality of initial castings, (3) preheating conditions for hot working, (4) dimensional control in hot working, (5) surface condition of the hot-worked product, (6) surface improvement processes, and (7) subsequent cold-working operations.

If conditions are unsatisfactory in preceding operations, then the final product may be of poor quality, notwithstanding perfect control in the final heat-treatment and finishing stages. All the above factors

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cannot be dealt with in detail, but it is proposed to refer to them briefly, since previous symposia have not covered these points for wire and rod products.

1. CHOICE OF FABRICATION METHODS

In choosing fabrication methods, the usual alternatives are extrusion and rod-rolling, with size and shape of casting as the next points to be settled, followed by a decision on the size to which the hot-working stage is to be taken. In general, extrusion results in a superior surface condition, though there are reservations to be made in this respect. Extruded rods generally have a coarser structure than rolled rods, resulting in lower tensile properties after drawing; this effect is not great with copper, but is serious with aluminium. While the size of the casting is governed by the plant available, its shape is a matter calling for considerable thought, at least in the case of copper wire-bars. The available types are horizontally cast tough-pitch bars, horizontal bars with the set surface removed by scalping, and vertically cast bars; the relative merits of these in respect to ultimate surface quality and mechanical properties have been much debated. The size of the hot-worked product is of major importance from the present aspect, because the larger the size, the greater is the possibility of eliminating surface defects arising in hot working, if only by the mere effect of spreading the work over a larger area. It is surprising how successful this sometimes proves, though it will be understood that, in general, products that are unsatisfactory at the hot-worked stage yield unsatisfactory final products.

2. QUALITY OF INITIAL CASTINGS

Surface condition is the feature mainly involved, it being assumed that the composition and shape of the casting are satisfactory. While it is not intended to labour the importance of casting quality, the main point to be made is that such faults as "sloppy edges" on horizontally cast copper wire-bars result in longitudinal seams in the finished wire, with consequent inferior properties, while in the case of vertically cast wire-bars, cracks in the castings can give somewhat similar seams and spills.

3. PREHEATING CONDITIONS FOR HOT WORKING

It is not always sufficiently appreciated that several pitfalls await the fabricator at this relatively simple stage. Control of temperature, control of atmosphere, and avoidance of damage in transfer or conveyance are the most important points for attention. The first two are fairly obvious because of their relationship to the amount of oxidation which will occur. In the case of copper, this is a serious matter both financially and from the point of view of quality. On the other hand, it is essential to avoid reducing atmospheres at this stage, because of their gassing effects on tough-pitch copper. For this reason, it is preferable for the furnace atmosphere to have an

oxygen content of the order of 1-2%; the oxide scale formed on such products as wire-bars is then well under 1%. With this amount, the scale is mainly detached in rolling, though the final hot-rolled wire-bars usually have 0.3% of oxide still adhering, which must be removed by pickling. When extrusion is undertaken the oxide scale adhering to billets may cause serious defects in the extruded product, such as sub-surface inclusions; actually in the case of extrusion, atmosphere control is of even greater importance in regard to quality than it is in the case of rolling.

Damage to products in the course of transfer through furnaces mainly occurs by the pick-up of ferrous-metal particles and of refractories from the skid rails, roof, or other parts of the furnace; pick-up can also occur in rolling. Inclusions become of increasing importance in the drawing of wire to fine gauges, there being a general relationship between wire breakage and the presence of inclusions, more particularly those of a ferrous nature. Hence, it is fundamental to take the utmost precautions to avoid the pick-up of harmful materials during preheating.

4. DIMENSIONAL CONTROL IN HOT WORKING

One major point to be stressed in the hot rolling of rods is that there must be accuracy of all the individual roll passes, so as to avoid the formation of fins at any stage. Fins can be formed at any of the 14-20 passes customarily employed in the rolling of copper and aluminium wire-bars into $\frac{1}{4}$ - $\frac{3}{8}$ -in.-dia. rods. The incidence of fins is not a function of the reduction per pass—which sometimes exceeds 50% in the early stages of working copper—but is dependent on the settings and on the constancy of section and temperature. If fins are allowed to form to any great extent, they fold over to give longitudinal-type seams; on subsequent drawing, these may form detachable slivers, which are equally, if not more, objectionable. This applies to both copper and aluminium, and indeed to all metals.

5. SURFACE CONDITION OF HOT-WORKED PRODUCT

The general surface condition of rod depends on the extent of pitting of the rolls. Some degree of roughness is inevitable, but this must not be allowed to develop unduly, particularly if only a small amount of cold work is to be applied later, because in this event the roughness persists in the finished product. In any case, pitted rolls tend to give a product with the oxide well rolled in, and correspondingly difficult to remove by pickling.

6. SURFACE-IMPROVEMENT PROCESSES

The pickling of hot-worked copper is essential before drawing, whereas aluminium is not pickled. The standard pickling solution for copper is sulphuric acid, and its use must be followed by washing and hosing to remove adherent copper dust, which remains on the metal as a result of the reaction between the oxide and

the acid. Any residual copper dust on the rods tends to give a dusty final product, and this may be detrimental in subsequent operations, such as enamelling. More serious is a failure to remove scale effectively in pickling, though this seldom occurs, except when grease is present on rods. This brief reference to pickling may, perhaps, end with a plea for more careful control of the operation, which is well worthy of investigation from many aspects.

Obviously conventional pickling is only "skin deep", and for the complete eradication of surface faults more severe measures are necessary. Among these are: (a) pickling in oxidizing acids, (b) rough annealing in normal atmospheres, (c) rough annealing in atmospheres which give accelerated oxidation, and (d) shaving of the surface to remove about 6% by weight from the rods. The virtues of some of these processes have been reported on and compared recently,¹ and there seems little doubt that the processes will be used to an increasing extent in the drive for higher-quality products. The only disadvantage is the increased cost.

7. SUBSEQUENT COLD-WORKING OPERATIONS

The cold-working operations on rod and wire products are responsible for the "finish" of the latter, provided that other factors are under satisfactory control. Lubricants, die condition, die material, and condition of the capstans are all of importance, but, beyond stressing this, it is difficult to lay down definite standards. Enough has been said already to indicate the considerable degree of interrelation between the various factors in the early processing operations, all of which affect the quality of the final product.

III.—OUTSTANDING CHARACTERISTICS OF COPPER IN RESPECT OF ANNEALING

Copper has a comparatively low annealing temperature, i.e. usually between 200° and 400° C., depending on many factors, and it possesses a high oxidation rate. Hence, although the metal can be annealed at low temperatures, it is necessary to protect it against oxidation during industrial annealing operations, unless it is desired to grow an oxide scale in order to remove surface defects, a practice which is sometimes adopted in early process anneals. In addition, in final annealing operations the presence of sulphurous atmospheres must be avoided to prevent sulphide tarnishing.

With the tough-pitch varieties of copper, the gassing reaction which occurs between cuprous oxide and hydrogen becomes of serious importance at temperatures much in excess of 400° C.

As copper can be pressure-welded with the application of only slight amounts of pressure at elevated temperatures in clean atmospheres (possibly slightly reducing atmospheres are necessary), a pronounced tendency to "stickiness" occurs in adjacent turns of

wire. This is very serious when it occurs, and the problem is discussed in more detail in Section V.

1. OXIDATION CHARACTERISTICS OF COPPER

The oxidation of copper has been investigated on numerous occasions, and an extensive bibliography has been compiled by Tylecote,² who, in a further paper,³ has published the results of an experimental study of the process. The oxidation rate follows a parabolic curve, and although increments in weight due to oxidation are very small below 400° C., pronounced discoloration occurs at 200° C. and upwards. Indeed, the discoloration can be appreciable at temperatures little above atmospheric, though normally in this case it is due to traces of sulphurous gases. The oxide films formed at low temperatures are, to some extent, protective against sulphide tarnishing.

Because of the considerable amount of oxide which forms at 600° C. and upwards, the industrial "rough annealing" of copper wire-rods is undertaken so as to shed a scale comprising the top 0.0005 in. or so of the rods. This scale carries a large number of rolled-in copper particles produced from the fins which form in hot rolling. The copper which is so oxidized amounts to about 0.5% by weight in the case of 0.25–0.35-in.-dia. rods.

In the Oxoff process developed by the Anaconda Wire and Cable Company,⁴ the introduction of certain chemicals, in particular halide salts, when oxidizing by heating above 600° C., results in the formation of a much heavier scale. This scale may represent 1.0% of the rod weight, an amount which is of much benefit in eliminating faults in the rod.

It will be appreciated that the above-mentioned rough-annealing processes are recognized as distinct commercial operations, and that the objectives are quite different from those normally sought in annealing to remove work-hardening effects.

2. RECOVERY FROM COLD-WORKING EFFECTS

The annealing of copper rod and wire is generally undertaken with the sole object of removing the effects of cold work, so as to attain the soft condition required for specification purposes or for further cold working.

The annealing characteristics of copper have been much studied, and the fundamental importance of the amount of cold work, prior grain-size, and time and temperature of the process, is widely appreciated. The presence of impurities has an enormous effect, Fig. 1 shows annealing curves for two commercial varieties of high-conductivity copper; these are the normal high-conductivity type of high purity, i.e. over 99.99% copper + oxygen, and a silver-bearing type containing 0.05% silver. These curves probably represent the extremes which are encountered, and all varieties or brands of high-conductivity copper will have annealing curves between these two limits. Particularly noteworthy is the steepness of the annealing curves, which indicates the impossibility of obtain-

ing the partly hard condition by letting-down from the hard state. It may be emphasized at this stage that temperature is the most important factor in annealing, and that the influence of time is really quite small, as shown in Section V, where it is mentioned that one industrial process anneals copper wire in a fraction of a second.

The effects of individual impurities on the annealing temperatures of copper have been included in the investigations of Smart and Smith,⁵ who used super-purity metal. Table I gives a summary of their

TABLE I.—*The Effects of Small Amounts of Impurities on the Softening Temperature of High-Purity Copper (Smart and Smith⁵).*

Addition Element	Softening Temp. (°C.) of Copper Containing the following Percentages of Addition Elements				
	Nil	0.001	0.005	0.01	0.05
<i>Oxygen-Free Material</i>					
Antimony . . .	140	160	280	320	340
Arsenic . . .	140	160	190	205	240
Cobalt . . .	140	145	150	160	160
Cadmium . . .	147	160	250	310	350
Iron . . .	142	143	...	162	167
Nickel . . .	140	...	137	...	141
Phosphorus . . .	140	235	280	300	...
Silver . . .	140	150	170	210	300
Sulphur * . .	136	220	231	224	...
Selenium * . .	137	245	292	303	307
Tellurium * . .	143	220	344	370	385
Tin . . .	137	150	277	315	347
<i>Tough-Pitch Material</i>					
Selenium * . .	146	227	282	290	295
Tellurium * . .	140	220	332	371	377
Tin . . .	138	143	137	143	141

* The materials were originally subjected to a high annealing temperature before cold working so as to obtain maximum amounts of selenium, tellurium, and sulphur in solid solution; the penultimate annealing temperature has a most marked influence.

results, from which the importance of minute amounts of impurities will be apparent. The softening temperatures recorded are those necessary to achieve the half-hard point in 1-hr. annealing periods. The half-hard point is defined as the mean of the tensile strength in the hard state and that after annealing at 500° C., and thus falls on the steep part of the curve; therefore in some cases, the temperature given is well below that required for complete softening.

In considering the results of Smart and Smith, it must be borne in mind that all commercial brands of high-conductivity copper contain small amounts of several impurities, whose effects on annealing characteristics are substantial. In the best brands of primary copper, there are amounts of about 0.0005–0.002% of each of six to ten impurities, and the data of Smart and Smith may be used to appraise the effects of each of these on annealing characteristics. Of those elements normally present, the ones having the greatest effect are tellurium, selenium, antimony, arsenic, sulphur, and silver. Thus, while Smart and Smith report a softening temperature of about 140° C.

for their super-purity copper, it can be expected that none of the commercial varieties will have a softening temperature below the value of 200° C. indicated for

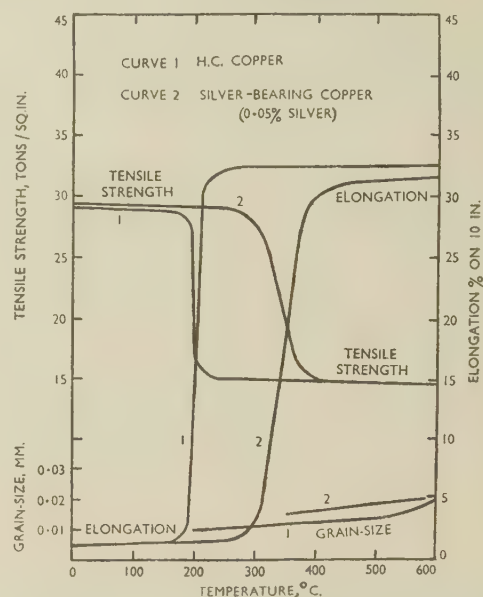


FIG. 1.—Properties of Copper Wire (Drawn to 94% Reduction) Annealed for 1-Hr. Periods.

one of the materials in Fig. 1. The softening temperatures of other less-pure varieties can be assessed from an accurate knowledge of their composition.

3. ELECTRICAL CONDUCTIVITY OF COPPER

The attainment of the necessary electrical conductivity involves less difficulty than do other properties. The basis copper accords with the specification requirements for conductivity if the impurities are sufficiently low, and normally the range encountered with commercial brands of high-conductivity copper is from 100.0% to as much as 101.8%; higher figures are rare, but specially prepared metal—as employed by Smart and Smith—has a conductivity of 102.4%.

The conductivity of commercial copper in the annealed condition is not sensibly affected by fabrication procedures. However, fabrication practice has an influence in the case of commercial high-conductivity coppers carrying small amounts of sulphur, selenium, and tellurium. If these types are heated to a high temperature and quenched, the conductivity may be several per cent. below specification requirements, because in this case the impurities are taken into solid solution.

Commercial, oxygen-free copper has a slightly lower conductivity, i.e. about 0.5% lower, than metal of the same purity in the tough-pitch condition, because the minute amounts of certain impurities, e.g. iron, exist in solid solution instead of in combination with oxides, and also there is a higher sulphur content.

Apart from the foregoing interesting points of detail,

which are normally kept well in mind during fabrication, the only matter concerning conductivity which arises is the reduction due to cold working (i.e. of the order of 3% for normal reductions), and the subsequent recovery after annealing. This point is allowed for in all published specifications. Hence the lower electrical conductivity of copper in the hard-worked condition presents no problem from the point of view of control.

Slight work-hardening effects on wire products, such as are introduced by rewinding processes, or even in straightening and slightly stretching wires before testing, cause an appreciable reduction of conductivity. The author has known cases in which copper wire of about 0.025 in. dia. has had its conductivity reduced by 0.5% merely by straightening and slightly stretching for testing purposes. As a result, material may erroneously be reported as failing to comply with the conductivity specification for annealed copper. Actually, conductivity is probably more sensitive to the effects of cold work of this nature than any of the mechanical properties, and it is one aspect of control of testing procedure which requires more attention than is at present given to it.

IV.—INDUSTRIAL ANNEALING PROCESSES FOR COPPER WIRE

Section III has indicated that the fundamental requirement in the annealing of finished wire is to avoid damage by oxidation and staining. There are many different and competitive industrial annealing methods which achieve this. Five different kinds of operation will be described.

1. WATER-SEALED BRIGHT-ANNEALING FURNACES

Furnaces which depend on the protective value of steam atmospheres have been in use for approximately 50 years and, at the present time, they still retain their popularity for the annealing of a large proportion of the heavier gauges of copper wire, &c., because they are cheaper in installation and operating costs, while the product is satisfactory for many requirements, and indeed, in some respects, is considered superior. The most usual type of furnace is based on the original Bates and Peard design, in which a chain conveyor carries the products to be annealed through a heated tube having water-seals at each end. There are modifications of such furnaces, mostly having the tube built vertically or at an angle of 30°, with a water-seal at the exit end only.

The tubes of all these types of furnaces generally comprise several cast-iron sections which are refractory-covered in the heated zone. The steam atmosphere is generated at the exit end when the charge enters the water-seal, so that this gives a positive

steam pressure which serves to counteract the tendency for furnace gases to enter through leaks in the tube.

With wire in coil form, and also wound on reels or spools* having a diameter exceeding 0.050 in., it is the general experience that the products dry off without staining when removed from the hot water. With some wire products, these furnaces are used for sizes down to 0.020 in. dia., though in this case there is noticeable staining. A disadvantage of the process is that the water tends to become dirty, so increasing the liability to cause staining; a helpful procedure to overcome this is to add tartaric acid or a tartrate.

2. DRY BRIGHT-ANNEALING FURNACES

The modern types of dry bright-annealing furnaces have evolved by a series of stages from the "sealed pot", which at one time provided the only means of dry bright-annealing. At present there are two types, batch and continuous, and these require separate consideration.

(a) Batch-Type Furnaces

The batch types almost invariably involve electrical-resistance-heated furnaces of 0.5–4 tons' capacity, with cognate equipment, and they are of either the "bell" or the "pit" type. It is essential to have a number of charge platforms or pots for each furnace, so that there is sufficient capacity to allow for the charging and cooling periods. Controlled gas atmospheres are essential throughout the heating and cooling periods; the individual charges must be effectively purged before heating begins. Either the pots are taken to the furnace or the furnace taken to the pots. Heating times may range from 2 to 4 hr. and cooling times from 6 to 12 hr., depending on the capacity of the equipment. The temperatures attained in the annealing of wire are generally in the range 300°–450° C. as shown on the control pyrometers. The latter indicate higher temperatures than are reached by the charge itself, and it is essential to evolve suitable control temperatures, heating times, stacking methods, and weights of charges for particular furnaces. Although no rule can be laid down, obviously a sufficient "head" of time and temperature must be allowed for the heat to penetrate the heaviest individual spools or coils comprising the charge. It is common practice to anneal wire on 600-lb. spools and sometimes 2000-lb. spools, which represent very compact masses of metal.

These furnaces all employ controlled atmospheres, and to a large extent the technical control of annealing centres round the preparation of such atmospheres, which are obtained from the combustion of town gas or of cracked ammonia under controlled conditions. The town gas, after mixing and burning, is cooled to remove most of the water and sulphur dioxide

* "Spool" is the conventional British term for describing the flanged, cylindrical metal containers on to which wire is wound in the course of drawing, this being in accordance with

the definitions in British Standard 1420: 1947.

"Reel" is the usual American term. Throughout the remainder of this paper the term "spool" will be used.

vapours, then passed over iron oxide to remove sulphides, and finally dried; a typical final composition is nitrogen 87, carbon dioxide 10, carbon monoxide 2, and hydrogen 1%. With the use of cracked and burnt ammonia, a typical final gas composition, after removal of water, is of the order of 96% nitrogen and 4% hydrogen.

The annealing of copper wire in these types of equipment, with the controlled gas atmospheres mentioned, is undertaken with generally satisfactory results, though rejection sometimes occurs owing to discoloration of the outer turns (caused by ingress of air), and there is the problem of "stickiness". The latter is undoubtedly a form of pressure-welding which occurs when tightly wound reels of wire are heated to 300° C. or higher. This is further discussed in Section V.

In annealing operations at temperatures exceeding, say, 450° C. on the control pyrometers (or 350° C. metal temperature), such as are necessary for annealing moderately cold-worked tough-pitch copper products, there is a danger of obtaining the well-known gassing reaction between tough-pitch copper and hydrogen. At such temperatures this occurs superficially, and indeed there is doubt whether, under the conditions existing, i.e. vapours from lubricants plus hydrogen, there will be any definite surface-gassing attack at temperatures less than 400° C., which is normally regarded as the minimum necessary. The occasions on which this trouble is encountered are rare, but the need to maintain temperatures within safe limits must be appreciated.

Another trouble that may arise in the bell or pit types of bright-annealing furnaces is volatilization of lubricating oils and their deposition on other parts of the charge, with subsequent decomposition to form hard carbonaceous deposits. This is not experienced with copper wire which has been drawn with the conventional soluble oil/water lubricants, but is occasionally encountered with strip material drawn or rolled with mineral oils. Possibly this occurs only when certain catalysts are present. The circulation of the gas atmosphere is a critical factor in this problem, though the ultimate solution lies with the correct choice of lubricants.

(b) *Continuous Furnaces*

Continuous bright-annealing furnaces of the "tunnel" type, with a series of trays carrying the metal charges, have recently been developed. At least three forms of such furnaces are used. In the first type, the furnaces are electrically heated, and supplied with a controlled atmosphere; in the second, the units are heated by the direct combustion of high-purity gas, which also provides the necessary atmosphere in the furnace; while in the third, there is a combination of electric and gas heating, with the products of gas combustion providing the atmosphere.

With the first type, the atmosphere control is on conventional lines, but wastage is considerable because of the comparatively large apertures at each end of

the line. With the other two types, in which the products of combustion are admitted direct into the furnace, use is made of the heat evolved in combustion, in addition to the application of the gases for control of atmosphere; this is advantageous from the point of view of thermal efficiency. Obviously the purity of the gas is of major importance, since there is no opportunity of eliminating sulphur or other harmful ingredients. Therefore it is necessary either to use a high-purity fuel, or to employ methods of reducing the sulphur content to tolerable amounts. Both procedures have been applied with considerable success. However, there are outstanding problems associated with staining and with the deposition of condensation products on to the annealed metal in the cooling zones; these are currently overcome on most plants by such simple procedures as partially enclosing the charges, or by providing protective hoods in the cooling zones. The admission or circulation of the gas atmosphere so that the general flow is in the direction opposite to that of the charge is also helpful.

Although the tunnel-type furnaces represent an advance from the point of view of mechanization and economy of operation, it would appear that, as yet, the overall control of quality is less satisfactory than in batch-type furnaces.

3. VACUUM-ANNEALING FURNACES

Bell-type electric furnaces which operate under near-vacuum conditions, namely about 5 mm. pressure, have recently attracted much interest. It is clear that evacuation is cheaper than the manufacture of a gas atmosphere, though the initial costs of the plant are higher because heavier hoods are necessary, which also means that power consumption and other running costs will be greater. The important advantage claimed for such furnaces is the avoidance of the welding of wires, there being no tendency to stickiness between adjacent turns of wire even with tightly wound spools. The annealed products have a satisfactory colour, because, although it is impossible to attain complete vacuum, the small amount of oxygen present is insufficient to form objectionable oxide films.

Owing to the limited experience so far obtained with this equipment, it is not possible to say whether all the claims made for it will be finally substantiated.

4. TUBULAR TYPES OF STRAND-ANNEALING FURNACES

Tubular types of strand-annealing furnaces are not in extensive use because they occupy much space, the speeds are limited, the thermal efficiency is low, and costs tend to be high. Strand-annealing undoubtedly gives excellent results, and indeed it is claimed that the ductility of its products is superior to that obtained by other methods. Certainly the wire receives more uniform heating than is possible with batch practice, where it is inevitable that the outer material

is at high temperature for several hours longer than the inner material.

This method of annealing has been applied on an extensive scale in conjunction with certain further processing operations on copper wire, especially enamelling. Indeed many such processes lend themselves very well to such application, because low speeds are involved. Thus, many enamelled-wire producers base their practice on the purchase of copper wire in the hard condition, and undertake annealing in tandem.

The equipment includes either an electric or gas-heated tubular-type annealing plant with the requisite number of heated tubes, which can be located in either the horizontal position or the vertical position, whichever is more convenient in relation to the remainder of the plant. The wire sizes for which such equipment is employed range from about 0.020 in. upwards. Naturally, such strand-annealing equipment must incorporate an atmosphere control and also a cooling section in order to obtain annealed material of satisfactory condition. Nothing elaborate in the way of technical control is necessary with such equipment, other than the maintenance of satisfactory atmospheres and reasonable temperature control.

Another use of tubular-type furnaces is in tandem with tinning, in which case, also, the speeds are convenient, i.e. 300–600 ft./min. There are advantages in this case resulting from the conservation of heat which is possible. The system has not been widely used, however. The major problem is inherent in attempting to synchronize two essentially independent processes.

5. STRAND-ANNEALING IN TANDEM WITH DRAWING

Considerable interest has been displayed in this method of strand-annealing, and although a number of different methods of heating have been tried, the author believes that the only commercially successful process is based on electric-resistance heating.

Three different versions of one proprietary machine are available for the annealing of wire ranging from about 0.16 in. dia. down to 0.004 in. dia. at speeds of 2000–5000 ft./min., depending mainly on the gauge of wire. With all three types the wire, after leaving the drawing capstan, passes over a number of electrical contact pulleys, which are conveniently located so as to provide the necessary length of travel for the electric-resistance heating. In the first section of the apparatus, the wire is preheated to a temperature of, say, 150° C. in air, but in the final zone, the wire is passed into a vertical or inclined steel pipe, the lower end of which is in a trough of water, so that a steam atmosphere is generated by virtue of the quenching of the hot wire in the water. The wire is dried before being wound on spools.

Annealing units of this type are particularly well suited to the annealing of copper wire in a wide range of gauges, because considerable latitude can be tolerated with regard to the temperature that the wire

attains. This follows from the fact that copper, unlike many alloys, does not undergo appreciable grain growth over the temperature range involved. The necessary protective atmosphere is generated in the steel tube, so that this is automatically controlled. Hence, provided that the various units are used only for the size-range suitable, very little in the way of technical control is required.

V.—DEFECTS DUE TO ANNEALING, AND THE TESTING OF COPPER WIRE

1. WELDING OR STICKINESS OF WIRE IN ANNEALING

The welding of adjacent layers of copper wire is one of the most troublesome defects that can arise when annealing copper wire in dry bright-annealing furnaces. The conditions under which welding occurs are fairly critical, and among many factors which must be considered are: (a) the type of copper, (b) the contact existing between adjacent layers, (c) the use of high temperatures, (d) the reducing-gas atmosphere, (e) the presence of a slight oxide film on the material before heating, so that a film of reduced copper is formed, and (f) the presence of lubricants on the wire.

It has been established that oxygen-free, or de-oxidized, copper is much more susceptible to welding than are other qualities of copper, though the reasons for this are not clear. The contact pressure of adjacent layers is very critical, tight winding leading to welding, whereas slack winding avoids it. The use of high temperatures is harmful.

It is significant that welding is never experienced when using steam-atmosphere bright-annealing furnaces, even though the wire may be extremely tightly wound on spools. Another significant point is that welding does not occur in the vacuum-type, dry, bright-annealing furnaces. The conclusion is therefore that furnace atmosphere plays a prominent part. Whether factor (e) is important is open to question, but when the annealing process yields metal with the slightly matt pink colour or "bloom" which is characteristic of freshly reduced copper, there is more danger of welding. Fig. 2 (Plate XXXII) is a photomicrograph through a typical "sticky" zone between two wires of oxygen-free copper, and it will be noticed that the wires are bridged by common crystals.

2. THE GASSING ATTACK

Undoubtedly one of the most serious defects of tough-pitch copper is the gassing attack which occurs when the metal is heated in reducing-gas atmospheres with hydrogen present. Gassing manifests itself in varying degrees and in many different ways. Although the phenomenon is normally under effective control in annealing operations, there are some occasions when unusual effects are experienced.

One such instance is the production of metal having a highly reactive surface condition (though without

showing deterioration of mechanical properties), which is linked with the slight "bloom" which has been mentioned previously. The metal can be described as being excessively clean, and in this condition it is very susceptible to subsequent sulphide tarnishing. Stocks of finished wire, after satisfying stringent inspection and in some cases after being rewound, have been known to develop internal black stains on subsequent storage in normal works' atmospheres. This staining effect may take months to develop. Fig. 3 (Plate XXXII) shows a photograph of a reel of fine-gauge copper wire which had developed black stains half-way through the reel, more pronounced on one side than the other; the stains are confined to the centre portions of the reel, it being noticeable that the black stains ceased at $\frac{3}{8}$ in. from each of the flanges. The theory advanced to explain this phenomenon was that the clean wire in the highly active condition was able to develop thin invisible protective oxide films on the outer surface layers, and again near the flanges, but that the inside material did not develop such oxide films; on subsequent storage in a sulphur-contaminated atmosphere, the clean unoxidized wire was directly attacked to form sulphides, whereas the slightly oxidized wire resisted this attack.

The above is not the true gassing attack, and apart from a few instances where this is experienced in bright-annealing furnaces—owing to ineffective control of the gas atmosphere, together with the lubricants actually on the metal, and the temperature attained in the process—it is the users who experience the greatest number of cases of actual gassing. In the further processing operations carried out by users, heat frequently has to be applied, as in brazing, silver soldering, hot bending, and annealing, and such heating is frequently effected by oxy-coal-gas or other flames which are played directly on the metal. Although these flames may appear quite harmless, they are often reducing in certain parts. Hence it is not always realized that damage has been done to the copper, and the products are placed in service, with the result that failure subsequently occurs.

Fig. 4 (Plate XXXII) shows a portion of copper strip, which had been in service in an electric motor for several months before its failure in a fatigue-like manner, as evident from this photograph. The motor winding was of a complex shape, and the manufacturer had locally heated the metal so as to bend it into the required shape. It is clear that, in the course of this local heating, the copper had been superficially gassed and its properties thereby impaired. Development of the fatigue-like fracture followed directly from the fact that the metal had unsatisfactory mechanical properties, at least on the surface.

While the above has been selected as one example, there are many others which could be cited, such as those which occur as a result of silver-soldering operations on rotor bars of electric motors. These experiences all point to the necessity for a wider understanding of the gassing effects to which copper is liable.

3. MECHANICAL TESTING, WITH SPECIAL REFERENCE TO SPRINGINESS

Mechanical tests for copper and strip products, as defined in various specifications, are confined generally to tensile-strength and elongation values, though there are also practical tests, such as torsional twist, lapping, and bending.

In addition, manufacturers and users have devised other practical tests, in which attempts are made to simulate conditions that exist in particular applications.

One of the most persistent difficulties is the springiness of annealed wire. Such wire may be required for use in the bare condition, but more usually it is insulated with various dielectrics. In practice, the springiness characteristics in the insulated condition may bear no relationship to those in the bare condition as annealed, not only because of the work-hardening effects introduced in the insulation processes, but also because of the effects of the insulation. The former are discussed in Section VI.

The so-called springiness characteristics of annealed copper wire and strip in bare and insulated conditions are important in coil-winding and similar operations. A satisfactory definition of springiness does not exist, but the usual conception is the tendency to depart from any particular shape which is formed from the material by bending, winding, or similar operations. Such changes in shape affect the space factors. Obviously the property is related to the modulus and also the limit of elasticity of the material, and will depend very much on the effectiveness of annealing and particularly on the ductility values—such as elongation—which are attained after annealing.

Springiness tests are not recognized in specifications, but empirical tests have been developed. Specifications as a rule merely include figures for elongation and, for example, British Standard No. 128 requires values to be in accordance with the following:

Wire Diameter	Minimum Elongation on 10 in.
0.0076 in. and under	15%
Above 0.0076 in. and up to 0.020 in.	20%
Above 0.020 in. and up to 0.048 in.	25%
Above 0.048 in.	30%

Corresponding foreign specifications are similar or a little less stringent, particularly in the finer sizes. Annealed tough-pitch copper wire, which satisfactorily meets such specifications, can show considerable differences in behaviour in process operations and also widely different springiness values, when tests are made in accordance with the various empirical methods available.

Space does not permit of a full description of all the types of tests in use, but they are classified in the following groups:

(a) Mandrel tests, in which wire is wound a certain number of times around a mandrel while under a given tension, and the springback which occurs on release of the load is noted (Belden and B.I.C.C. test; see Fig. 5, Plate XXXII).

(b) Deflection tests, in which a straight length of wire is bent 90° around a mandrel, allowed to spring back to its natural position, and the angle of deflection noted (Moorhouse test; see Fig. 6, Plate XXXII).

(c) Stiffness tests, in which a straight length of wire is mounted in a holder and the latter deflected through 15° with the free end of the wire pushing against a loaded spring-gauge; the reading on the gauge is a measure of the stiffness.⁶

(d) Stiffness tests, in which a length of wire is clamped at one end, subjected to a bending force and the angle of bend measured.⁷

(e) Ductility tests, in which the elongation that occurs under light tensional loads is measured; the instrument measures the elongation occurring between tensional loads of 7500 lb./in.² and 15,000 lb./in.² (G.E. test).⁸

The readings obtained from methods (a), (b), and (d) are in degrees, and values obtained from such tests are frequently quoted. As the results depend on size of specimen, as well as the variation according to condition of the material and other factors, it is not easy to assess their true significance. Again, variation in results is encountered on a given material, and the curvature of specimens cut from coils or spools is important. Quite different figures are obtained according to whether the specimens are bent with or against their original curvature. The results of springiness tests by such methods depend very much on whether small amounts of cold work have been applied, such as are imparted in straightening. This matter is discussed below.

VI.—PROCESSING OPERATIONS ON COPPER WIRE AFTER ANNEALING

Although wire may be considered as a finished product from the metal-manufacturing aspect, it generally has to undergo much further processing before it emerges in the form of a marketable engineering product. However, it is intended here to confine the consideration of such intermediate processing operations to their effects on properties. Of foremost importance are (1) inspection, (2) packaging, and (3) rewinding.

Tinning is also a metallurgical process, but space does not permit of an adequate treatment of this subject. The other processing operations are those of insulation with such materials as enamels, cotton, silk, glass, P.V.C., &c., and in the application of these the major problem, from the point of view of metal characteristics, is that of the stretching of the wire, with consequent effects on its properties. Remarks made under sub-section VI, 3 will therefore be applicable to these further operations.

1. INSPECTION

Inspection of wire is of necessity limited to a visual examination of the surface layers, together with gauge and property determinations on the end portions. It is impossible to inspect the inner warps of

coils or spools, and hence it is always necessary for some control of quality to be undertaken in the earlier processes. As finishing wire-drawing speeds are upwards of 4000 ft./min., the examination, even then, is far from thorough. In fact, the practical wire-drawers' assessment of quality is based on the number of breakages which occur in drawing, and it is common experience that there is generally some connection between wire breakage and surface quality.

Even when wire surfaces are free from the more common faults of surface laps and spills, and are also free from copper dust, there are differences in surface standards which are incapable of real assessment. These differences arise from die condition, nature of lubricants, and other factors. There are no recognized tests which attempt to evaluate surface variations of this nature, and indeed this is greatly to be regretted. This problem is, however, recognized as one of considerable difficulty.

2. PACKAGING

Packaging procedure varies according to the weight and type of spool or reel. In the case of annealed copper wire on a steel spool—which is now the most popular and the cheapest form—the weights vary from 4 to 200 lb. or more. Such spools, after wrapping in paper, are packed in well-finished wooden cases for transportation. After the further processing operations have been carried out on the wire, the steel spools are returned to the wire-drawing department. They generally need some form of reconditioning—including flange-straightening—before further use. The treatment which spools have to withstand is quite severe, including distortion on heating during annealing, rusting from contact with water, and mechanical damage.

Where rewinding takes place, it is usual to rewind on to wood or plastic moulded reels; in some cases anodized aluminium reels are used. Plain copper wire has to be rewound on to such reels as a separate operation, and this is naturally a costly procedure, so that there has been considerable incentive to eliminate this practice. Tinned wire in fine gauges is usually supplied on plastic or wood reels. Again, such reels are usually delivered in wooden packing cases, though in some instances moulded papier-mâché containers have been employed for the packaging of a few reels, and these containers then packed in crude wood cases.

Another wire-packaging method is to use a cardboard drum-type container. Such plain containers have long been used for merely packing wire coils, but recently there has been much interest in the possibilities of applying containers for the reception of wire direct from drawing, tinning, enamelling, and similar processes.⁹ The method is applicable to wire of sizes such that the material is sufficiently stiff, say 0.020 in.-dia. upwards for wire in the soft condition or 0.015 in.-dia. upwards in the partly hard state. There is no limit to the size of pack, but the sizes chosen for convenience have been 400–600 lb. The speeds

for which the method is suitable mostly range up to 1000 ft./min., though higher speeds have been used. The wire, after leaving the capstan, is run through a guide or pipe into a special cardboard container which rotates at the same speed as the capstan; the wire is deposited into the container in an even manner and, when required, it pays out quite smoothly. The advantages from the point of view of storage and package of wire in such dust-free and damage-proof containers are considerable. The applications of this process have up to the present been confined to the packaging of lightly drawn steel, brass, and other metal wires from medium-speed drawing machines, and tinned and enamelled copper wire from tinning and enamelling machines. The process is not as yet applicable to the production of copper wire, annealed by conventional processes, though there are possibilities with strand-annealing.

3. REWINDING OPERATIONS

Annealed copper wire is a delicate product, and it is not always appreciated that even low tensional loads

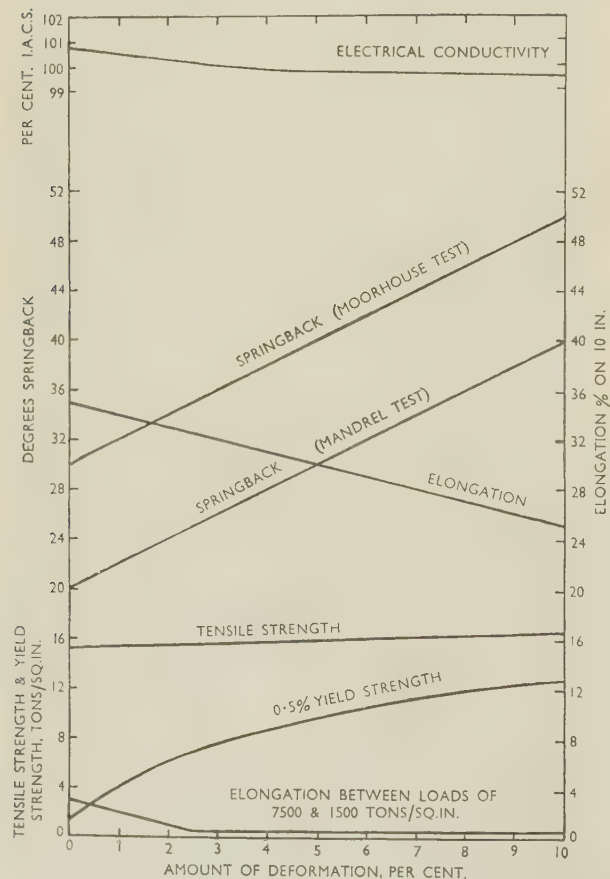


FIG. 7.—Effects of Small Amounts of Deformation on Properties of Copper Wire.

result in permanent damage. There is no doubt that many of the complaints concerning springiness of bare and insulated wire are due to damage through the use of unsuitable tensional loads. Bliss¹⁰ has pointed

this out in connection with enamelled wire, and his suggested maximum tensional loads are applicable to other copper products; briefly these are a maximum tensional stress of 3.5 tons/in.² on the finest wires, falling to 2.5 tons/in.² for sizes of 0.015–0.120 in. dia. These values seem to be slightly on the low side, but it is essential for the tensional stresses to be kept at little more than the limit of elasticity of soft copper. It is known that the tensional stresses present in some processing operations sometimes exceed 8 tons/in.², and hence it is not surprising that there are harmful effects on the metals. There is a great need for the use of tension meters, and it is gratifying to note that some industrial models have now been developed.

The number of rewinds should be kept to a minimum, because every straightening and rewinding operation inevitably imparts a small permanent deformation. In the natural course, but with extreme care, the deformation on rewinding and insulating by most processes can be kept within 2%, though this limit is often exceeded and some products may become stretched by 8%. The effect of deformation on some of the properties of annealed copper wire is shown in Fig. 7.

In operations on fast coil-winding machines, as employed in the electrical industry, it is necessary to wind with stresses exceeding the proof or yield stress of the material and also to impart a definite stretch, so that the coils will take on a permanent set, and thus avoid any tendency to spring open. The stretch which is imparted is sometimes in excess of 10%, but at this stage of processing, such deformation is unimportant.

VII.—THE ANNEALING AND OTHER CHARACTERISTICS OF ALUMINIUM WIRE

Many of the general observations which have been made in Sections III–VI are applicable to the processing of aluminium and aluminium alloy wire, but nevertheless there are a number of differences.

From the aspect of annealing and heat-treatment procedure, an important difference is that it is not necessary to provide special atmospheres, as aluminium and its alloys are not subject to gross oxidation effects; they form protective and tenacious oxide films on heating in air, which are, however, of limited depth.

1. ALUMINIUM WIRE

In general, the important industrial applications of aluminium wire involve the use of hard-drawn material, and, up to the present, there has been little demand for softened material. In consequence, annealing operations are mostly restricted to process anneals, and these are required only when reductions exceed about 94% in cross-sectional area or when special final properties are required.

Although there are several grades of commercial aluminium, the one which is of pre-eminent importance for wire production is the "electrical grade". As

the title implies, this is produced to a given conductivity standard and not to a specified composition; in addition, it is essential that the tensile strength should conform to minimum requirements. Hence the "electrical grade" usually has a composition of aluminium 99.5 min., iron 0.15–0.45, silicon 0.05–0.12%, with mere traces of other elements, particularly those which adversely affect conductivity or impair corrosion-resistance.

The only other grade of aluminium which need be considered for wire production is the super-purity type, which has recently become widely employed in

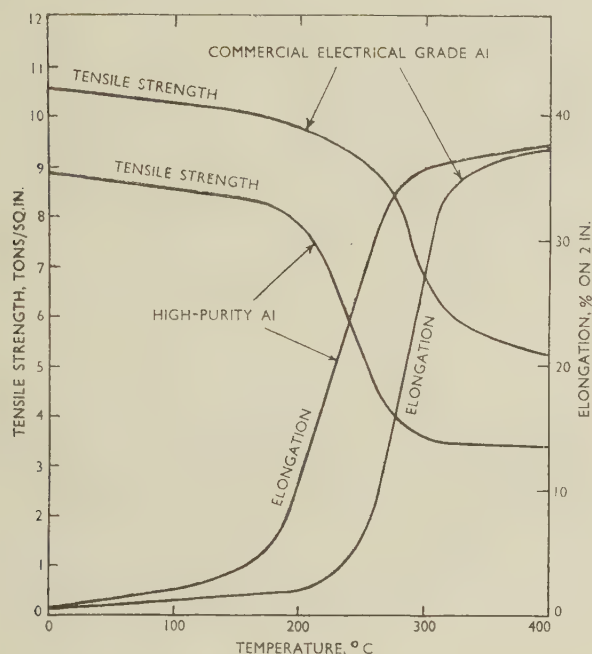


Fig. 8.—Properties of Aluminium Wire (Drawn to 94% Reduction) Annealed for 1-Hr. Periods.

the anodized condition for ornamental purposes such as costume jewellery.

With the electrical-grade material there is, as already noted, considerable variation of composition, but this does not cause inconvenience in production. Although the electrical conductivity of super-purity metal is of the order of 66%, the published specifications for electrical-grade material in the form of hard-drawn wire demand 60.6 or 61.0% minimum conductivity, with a somewhat higher minimum average for deliveries. The range encountered in industry is from 60.6% up to about 62.5%. In the annealed condition the conductivity is somewhat higher, say, by 0.5%. The variation of impurities accounts for the spread, and a number of studies^{11–14} have been made of the effects of such impurities. With certain combinations of impurities, particularly iron and silicon, the conditions of heat-treatment have an important effect on conductivity; the hot-rolling procedure and probably earlier operations also influence the result. For maximum conductivity there

is an optimum ratio of iron to silicon, and this appears to be 3 : 1. The relationships between composition, fabrication procedure, and conductivity are probably worthy of more study, though the differences involved are only small.

The temperature required for the annealing of hard-worked aluminium is affected by the impurities, and the form of the annealing curves for super-purity and commercial-grade electrical-quality aluminium are shown in Fig. 8.

The annealing curves have a gentle slope, in contrast to the steep slope existing for copper as shown in Fig. 1. For complete softening it is necessary to heat super-purity metal to a temperature in excess of 250° C., while for commercial-quality metal, the corresponding temperature is in excess of 300° C.

By careful control of the annealing temperature, it has been claimed to be possible to produce partly hard material, though it will be appreciated that this is rather difficult. However, this method of obtaining a desired temper may be of considerable help in the production of aluminium wire for insulated cables, where the properties required are more or less intermediate between the values in the annealed and those in the fully hard-worked conditions.

Annealing processes are carried out in a wide variety of furnaces, which are almost invariably of the forced-air-circulation type heated by gas or electricity. The temperature control must be sensitive, particularly for the purpose of partial annealing. In the latter case the method of stacking and other factors are also quite critical, but even with the utmost precautions, considerable variation in final results is experienced.

2. ALUMINIUM ALLOY WIRE

Alloys of aluminium, which are of importance in wire form, fall into two groups; (a) those for electrical purposes, and (b) those for general applications.

The first group is in practice confined to the aluminium-magnesium-silicon alloys, with about 0.5% each of magnesium and silicon, though recent developments have suggested the use of other alloys, such as the aluminium-magnesium alloys for applications involving flexure¹⁵ and the aluminium-magnesium-iron alloys for electrical rotor windings.^{14, 16}

The second group includes the aluminium-magnesium alloy with 2% magnesium and several of the harder heat-treatable aluminium alloys, in various conditions of temper as achieved by heat-treatment and cold working. These are mainly required for mechanical purposes.

In the case of both groups of alloys it is therefore necessary to employ solution-treatment, annealing, and precipitation-treatment. The exact requirements, and control methods necessary, differ with each alloy, but as a general rule they involve temperatures of the order of 520°–550° C., 330°–350° C., and 150°–200° C., respectively, for these three different types of heat-treatment.

For such heat-treatment operations, a wide range

of furnace types and sizes may be used, but there must be close control of temperature. Batch-furnaces, either gas or electrically heated, and provided with forced-air circulation, are usually employed. For the heat-treatment operations in the three temperature groups mentioned, separate installations are normally provided, because it is uneconomical and unsatisfactory to attempt to change temperature ranges frequently. As an alternative to batch-furnaces, salt-bath furnaces can be used, particularly for the solution-treatment stage.

3. OBSERVATIONS ON FURTHER FABRICATION PROCESSES

Inspection and packaging procedures vary considerably with the different types of product and the purposes for which these are required, though the principles are generally similar to those described for copper.

It is usual to supply on spools in the case of aluminium wire in the hard condition, and also in the annealed or intermediate condition, whether achieved by partial annealing or the application of a small cold reduction. As these products are almost invariably required for processing into some type of cable, this is the most convenient procedure.

With section wire, as required for motor windings, and with aluminium and alloy wire for rivet production and miscellaneous purposes, supply in coil form is mostly favoured, though reels are sometimes used.

All forms of aluminium in the annealed condition must be handled carefully to avoid damage by stretching or other deformation, because it will be appreciated that the strength properties are much

lower than with copper; therefore the comments made on the latter are more than ever applicable.

The electrical grade of aluminium wire has been marketed in the anodized condition.¹⁷ Care is necessary in the anodizing process and also in further coil-winding operations on the anodized wire, because the material cannot be stretched to any considerable degree on account of its low elongation and the brittle nature of the oxide film. This is a handicap, but not an insuperable barrier, to the wider use of the material. In place of anodizing it has been suggested that some form of chemical oxidation, followed by sealing with varnishes or other media, should be undertaken, so as to produce insulated wire having greater ductility than anodized wire. Experience with such products is limited.

Because there has been only a limited use of aluminium and aluminium alloy wire—apart from the important application for overhead conductors—techniques for some time are likely to remain fluid. This is true of the whole of the procedure involved in fabrication and related operations, as well as to the practice in the user industries. Thus there are wide fields of application open for investigation, and there is no doubt that many details of procedure remain to be finalized.

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REFERENCES

1. —, "Non-Ferrous Heavy Metal Fabrication in the U.S.A." (Technical Assistance Mission No. 79), pp. 58–63. 1954: Paris (Organization for European Economic Co-operation); London (H.M. Stationery Office).
2. R. F. Tylecote, *J. Inst. Metals*, 1950–51, **78**, 259.
3. R. F. Tylecote, *ibid.*, 327.
4. U.S. Patents Nos. 2,291,201 and 2,291,202.
5. J. S. Smart, Jr., and A. A. Smith, Jr., *Trans. Amer. Inst. Min. Met. Eng.*, 1942, **147**, 48; 1943, **152**, 103; 1946, **166**, 145.
6. L. B. Barker and C. A. Bailey, *Wire and Wire Products*, 1935, **10**, 375.
7. —, *Amer. Soc. Test. Mat., Standard No. B 113-41*.
8. Catalogue of General Electric Company of America.
9. —, *Wire and Wire Products*, 1954, **29**, (3), 273.
10. R. Bliss, *ibid.*, 1953, **28**, (3), 257.
11. A. J. Field and J. H. Dickins, *J. Inst. Metals*, 1933, **51**, 183.
12. G. G. Gauthier, *ibid.*, 1936, **59**, 129.
13. A. T. Robinson and J. E. Dorn, *Trans. Amer. Inst. Min. Met. Eng.*, 1951, **191**, 457.
14. R. H. Harrington, *Trans. Amer. Soc. Metals*, 1949, **41**, 443.
15. J. Hérenguel, Catalogue of Tréfileries et Laminoirs du Havre.
16. R. H. Harrington, L. B. Barker, M. F. Sayre, and C. H. Holley, *Metal Progress*, 1953, **63**, (5), 90.
17. H. Bardot, *Métaux, Corrosion-Ind.*, 1953, **28**, 19.

THE CONTROL OF QUALITY IN THE HEAT-TREATMENT AND FINISHING OF COPPER AND COPPER-BASE ALLOYS *

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SYNOPSIS

A number of special applications of heat-treatment are discussed with special reference to the heat-treatment of chromium copper and the use of low-temperature treatment for the removal of internal stresses. A description is given of the final processes of shearing, straightening, cutting to length, and removal of burrs, with mention of some of the effects of machine-straightening on the dimensions and mechanical properties of the material straightened. The controls necessary and the action to be taken in order to ensure a satisfactory product are considered in relation to the purpose for which the material has been manufactured.

The general procedure for inspection is discussed, and reference is made to mechanical, electrical, and hydraulic tests.

A section is devoted to the attention necessary to avoid damage, both mechanical and chemical, during warehousing and delivery of the material to the customer's works.

I.—INTRODUCTION

IN any metal-manufacturing concern a properly organized system of technical control of the quality of its products is a necessary aid to the efficient production of goods acceptable in all respects to the consumer. It is essential that products and processes are controlled through all stages of manufacture from the foundry to the warehouse. In addition, certain standard procedures need to be adopted in order to ensure that the products successfully withstand transit to the customer's premises.

Previous papers in this series of symposia have discussed the theoretical and practical implications of quality-control systems adopted in the earlier stages of production. It is the purpose of the present paper to outline the practical methods of exercising control of quality and to discuss some of the problems that arise in the heat-treatment and finishing processes in the manufacture of copper and copper alloy sheet and strip, sections, and tubes.

Although the assumption is made that products delivered to the heat-treatment and finishing departments comply with the relevant specifications, as far as applicable, with regard to chemical composition, mechanical properties, shape, and surface finish, the routine procedure adopted during the final inspection of materials is reviewed, and some of the material defects that may be revealed are discussed and illustrated.

The more important causes of deterioration of quality of finished products during transport to the

consumer are corrosion and mechanical damage. These are considered, and the final section of the paper deals with the methods employed to maintain the standard of finish achieved in manufacture.

II.—HEAT-TREATMENT OF COPPER AND COPPER-BASE ALLOYS

Heat-treatable copper and copper-base alloys fall into four main groups, requiring different equipment and techniques, which depend upon the material concerned and upon the physical and mechanical properties desired.

Reference has already been made by Kee¹ to the problems involved, and to the control necessary, in the case of a first group of materials required in the form of bright-annealed sheet and strip; for these use is made of furnaces employing controlled atmospheres. Some special problems of production relating to this process, which do not seem to have been previously discussed, are worthy of particular reference.

The second group of alloys—few in number but of increasing importance—the electrical and mechanical properties of which are capable of considerable enhancement by a combination of solution and precipitation heat-treatments, is described here in detail.

Certain other alloys, comprising the third group, particularly the complex aluminium bronzes in many of the forms normally manufactured, require heat-treatment to develop a satisfactory combination of mechanical properties.

The fourth and last group of materials is subjected

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to a low-temperature process designed either to remove internal stresses set up in the final stages of manufacture or to modify the mechanical properties of some groups of copper alloys.

1. CONTROLLED-ATMOSPHERE ANNEALING

The successful production of bright-annealed copper and phosphor bronze in sheet, strip, or wire depends, as described by Kee¹ and also by Hesselberg and Mantle,² not only on close control of the protecting atmosphere, but also on the use of low-flash-point lubricants which vaporize freely, leaving a stain-free surface on the furnace charge. Suitable lubricants which conform to these requirements are now generally available, but because of their essential characteristics, a secondary problem is inevitably introduced.

Coils or drums of wire and strip, and particularly the finer gauges of foil, are often tightly wound after the last pass. The adjacent layers of such coils are therefore in intimate contact and, as soon as the thin protective film of lubricant is removed by raising the charge in temperature, the naked surfaces will readily weld together if the peak annealing temperature is set too high. It appears likely that this phenomenon is a type of pressure-welding.

The incidence of sticking in coils of strip and wire annealed in batch-type controlled-atmosphere furnaces can be quite high when heat-treating phosphor bronze and phosphorus-deoxidized copper. This is probably due to the presence in both these materials of phosphorus; the latter seems to give rise to a surface condition in which cohesion occurs more readily than is the case with high-conductivity copper and phosphorus-free copper alloys. The frequency of occurrence can be reduced by employing the minimum of tension necessary to produce a satisfactory coil at the rolling, slitting, or drawing stage. Care must also be taken in the loading of coils of strip or wire in each furnace charge. The coils must not touch, nor be stacked on top of, each other and should preferably be annealed on a flat surface. To achieve these essential conditions in the bell-type bright-annealing furnace, a loading basket equipped with a series of well-supported grids is used. This permits maximum atmosphere circulation and ensures uniform annealing.

It is particularly difficult to achieve the annealing of high-tin bronze wire without a certain degree of sticking. The size of the coil must be taken into consideration, since with heavy coils the weight causes the bottom half of the coil to stick while the upper portion remains comparatively free.

It is important at all times to use the lowest adequate annealing temperature with a corresponding increase in soaking time if sticking is to be minimized. As an example, the annealing programmes shown in Tables I-III have proved satisfactory.

Although continuous or strand-annealing processes provide a reasonably satisfactory solution to this problem, it is necessary to ensure, by the provision

of unwinding equipment such as power-driven pay-off drums or wire-reel flakers, that the stress exerted on the section of foil or fine wire at the hottest part of the furnace is small enough to avoid stretching. If the stress is too great, the resultant reduction in cross-sectional area may well be great enough to render the material liable to rejection.

When strand-annealing phosphor bronze wire containing 7-8% tin, it is important to control the annealing temperature within close limits. If the wire is annealed at too high a temperature (over 700° C.) and, in addition, is subjected to the normal

TABLE I.—*Annealing Temperatures and Times for 7% Tin Bronze Wire.*

Dia., in.	Temp., °C.	Time, min.
0-008	400	75
0-010-0-014	410	75
0-014-0-018	430	75
0-018-0-030	450	90
0-036	480	90

TABLE II.—*Annealing Temperatures and Times for 5% Tin Bronze Strip.*

Thickness, in.	Temp., °C.	Time, min.
0-002-0-003	400	75
0-004	420	75
0-004-0-006	440	75
0-006-0-008	460	90
0-010	480	90
0-010-0-015	500	90
0-015-0-020	520	90

TABLE III.—*Annealing Temperatures and Times for Copper Strip.*

Thickness, in.	Temp., °C.	Time, min.
0-001-0-002	310	40
0-002-0-004	330	45
0-004-0-006	360	45
0-006-0-008	380	45
0-008-0-010	400	75
0-010-0-018	420	90

tensile stress necessary to convey it through the furnace, beads of tin sweat will form on the surface of the wire. The mechanism of this migration of copper-tin compounds from a homogeneous solution is not clear, but the magnitude of the applied stress and the working temperature appear to be important factors. This defect is eliminated by employing an annealing temperature of 650°-680° C. and adjusting, in accordance with the size of the wire, the speed at which it travels through the furnace. A chart showing the best operating conditions of the furnace for the range of wire sizes normally annealed should be prepared for the furnace operator's use.

The increase in density which occurs when severely cold-worked high-conductivity copper is annealed is well established. The difference is of the order of

0.1–0.2% only, and may be disregarded for most practical purposes. In the manufacture of rolled or drawn copper strip supplied in the annealed condition, however, this contraction in volume of the strip which takes place during annealing is not negligible if the permitted variation in dimensions of the strip is narrow. In the production of copper strip of nominal width 1.31 in. for the manufacture of co-axial cable, the contraction in width which occurs is of the order of 0.0004 in., and allowance for this should be made when preparing the cutters for slitting the hard strip before annealing.

Special precautions have also to be taken during the manufacture of certain types of copper tubes. Campbell³ has shown that the presence of carbonaceous films on the internal surface of tubes for domestic water supply can, under certain conditions and with some types of water, accelerate corrosion and result in early penetration. It is therefore necessary to adopt procedures which will prevent the formation of such films. It is generally accepted that carbonaceous deposits are formed when the residual films of lubricants of a high flash-point are cracked during annealing. While it is true that the old method of annealing in open (oxidizing) atmosphere furnaces followed by sulphuric acid pickling ensured freedom from these harmful deposits, such procedures are no longer attractive in modern methods of production, which are designed for the manufacture of very long straight lengths or coils. The finish-cleaning of such long lengths by conventional acid-pickling processes is particularly difficult. Annealing in modern controlled-atmosphere furnaces makes this unnecessary, but care must be taken to use the right type of lubricant if clean tubes are to be produced. There are a number of satisfactory lubricants available, and, so long as steps are taken to keep the residue left in the tube to a minimum, it is unnecessary to degrease before annealing.

For the finish-annealing of refrigerator tubes, the internal surface of which must be kept quite bright and clean, the normal procedure is to degrease, and to purge the coils of tube with burnt town gas or with cracked and burnt ammonia before annealing in these atmospheres.

2. HEAT-TREATMENT OF COPPER-BASE ALLOYS OF THE PRECIPITATION-HARDENING TYPE

The heat-treatment of this group of alloys is a conventional two-stage process: a solution-treatment at temperatures varying from 800° to 1000° C., followed by a water-quench, and a precipitation-treatment at temperatures varying from 350° to 500° C. Although the programme is simple, special precautions are necessary with some alloys to ensure a satisfactory product.

(a) Chromium Copper

This alloy is normally manufactured in the form of plate, bars, and rods for seam- and spot-welding electrodes. It is also used in commutators of electric

motors designed for special purposes to operate at elevated temperatures. The chromium content is usually controlled within 0.5–0.75% to provide a slight excess over the solid-solubility limit of chromium in copper of 0.4% at 1000° C.⁴

It is necessary to solution-treat chromium copper in a neutral or slightly reducing atmosphere. At the normal treatment temperature (1000° C.), chromium is preferentially oxidized if the heat-treatment is carried out in an oxidizing atmosphere. Fig. 1 (Plate XXXIII) shows the depth of penetration which can occur in 1-in.-dia. rod so treated.

Grain growth at these high temperatures is quite rapid. It is most important to determine the minimum time necessary to effect maximum solution of the chromium in order to avoid an unsatisfactorily large grain structure. This has been found to be important in the production of thin strips and commutator bars in which the thin edge is less than 0.080 in. thick. A coarse-grained commutator strip in the fully heat-treated condition will not respond satisfactorily to the final reduction in section which is usually made. A very uneven plastic flow results, and a rough and wavy surface appears at both thick and thin edges.

Two general types of heat-treatment furnaces are employed for the solution-treatment stage of chromium copper production: electrical-resistor and gas-fired batch-type furnaces with suitably controlled atmospheres are in general use, but the electrically heated salt bath, using a mixture of barium chloride, sodium chloride, and potassium chloride, is now more widely used. The principal advantage of this type of furnace is the rapid and uniform heating cycle. Operating temperatures can be controlled accurately, and there is usually a smaller range of temperature variation during the power-on, power-off cycle. In addition, the salt protects the charge from oxidation and results in a completely scale-free heat-treated product. In general, it is therefore possible to heat-treat chromium copper strip of small cross-sectional area without danger of overheating and with the use of a comparatively short cycle time (usually not more than 15 min.); excessive grain-growth can thus be successfully avoided. Salt-bath furnaces are not suitable for the high-temperature treatment of some chromium copper tubes. Particularly extensive cracks occur in thick-walled tubes of medium diameters, a typical size being $7\frac{1}{2}$ in. (outside dia.) \times 6 in. (inside dia.). The cracks are intercrystalline, and are presumably due to some form of stress-corrosion failure. This breakdown may be due to the internal stress present in the drawn tube before heat-treatment, but the cracking is not entirely eliminated even if the tubes receive a prior stress-relief treatment. Such tubes can, however, be successfully heat-treated in electric or gas-fired controlled-atmosphere furnaces.

In the production of forgings and some extruded sections in chromium copper, it is frequently possible to water-quench the product as it leaves the die, thus eliminating the need for a second reheating for the

solution-treatment. The temperature of the product must not be allowed to fall below 900° C., and preferably not more than a few seconds should elapse before the product enters the quenching bath.

As the high-temperature stage of precipitation-hardening is generally quite critical, it is important that the temperature-controlling equipment be examined frequently to ensure accuracy of operation. A routine check of furnace thermocouples against standards is most desirable, and a record should be kept of all recalibrations found necessary. In addition to this routine, samples are regularly taken for laboratory checks on the efficiency of the production process to ensure that the maximum physical and electrical properties are being developed. It is also necessary to ensure that there is an adequate circulation of cold water in the quench tank, and that the bundles of strip or coils are small enough to permit efficient and rapid cooling. This routine technical control is supplementary to that at the casting stage, where samples are taken from each cast for analysis and to determine that the hardening constituents are in a finely divided and dispersed condition, free from oxides and other compounds which may destroy their efficiency by rendering them unsuitable for, or incapable of, solution at the heat-treatment stage (Fig. 2, Plate XXXIII).

As, in a general way, the secondary or precipitation-treatment stage is not so critical, the controls necessary need not be so stringent. A conventional batch-type electric furnace equipped with forced-air circulation is generally used, but atmosphere control is not obligatory. For chromium copper, a temperature of 475° C. is normally employed, with cycle times of the order of 4 hr., the exact time depending upon the form of the furnace charge. Regular checks of the accuracy of the equipment controlling the furnace temperature are desirable, and the employment of temperature-recording equipment provides a satisfactory check on this part of the heat-treatment programme. At

Table IV shows the results of three typical mechanical and electrical tests made on fully heat-treated and drawn chromium copper of different sections. The heat-treatment consisted of a preliminary solution-treatment at 1000° C. for 15 min., followed by precipitation-hardening at 475° C. for 4 hr.

(b) *Beryllium Copper*

Many of the precautions and controls necessary for the successful production of chromium copper are equally important in the manufacture of beryllium copper. Although the solution-treatment temperature of 800°–840° C. is substantially lower than that necessary for chromium copper, a certain degree of superficial oxidation occurs unless a protective atmosphere is used in the furnace. As the depth of penetration is not so great, it is possible to remove any black oxide scale which may be formed by pickling in a sulphuric acid solution. The solution of beryllium in the 2% beryllium alloy is complete only at 800° C.,⁵ and care must therefore be taken to verify the accuracy of the furnace-control equipment by regular checks against standard thermocouples. At the precipitation-hardening stage, accurate temperature control is again necessary, together with standard cycle times which will vary according to the alloy composition and the physical condition of the batch. More complete details of the heat-treatment of these alloys have been published by the Copper Development Association.⁶

(c) *Copper-Nickel-Silicon Alloy*

Material in the form of forgings and extruded or rolled bars is generally manufactured to comply with the specifications D.T.D. 498 and D.T.D. 504, having a tolerated composition range of 2.0–2.6% nickel and 0.4–0.8% silicon. In all forms, the alloy is normally supplied in the fully heat-treated condition which involves a two-stage process, and the necessary controls to ensure the production of satisfactory material are similar to those described previously.

The following mechanical properties are typical of those possessed by this alloy in the form of 1-in.-dia. rod extruded and heat-treated at 900° C., quenched in water, and tempered for 2 hr. at 530° C.

Ultimate tensile strength, tons/in. ²	40.5
0.1% Proof stress, tons/in. ²	32.0
Elongation, % on 2 in.	17

Similar properties may be obtained on forgings, but it is of interest to note that although the solution temperature may vary from 850° to 900° C., the precipitation-treatment temperature must be controlled within the limits 520°–540° C.

In addition to the precautions mentioned above, it is essential to control the grain-size of forgings and extrusions before the solution-treatment. Material having a large grain-size will frequently be in a very brittle condition after heat-treatment, probably as a result of the tendency for the hardening constituent to separate out at the grain boundaries.

TABLE IV.—*Properties of Wrought Chromium Copper Fully Heat-Treated and Cold Worked.*

Reduction of area 25%.

	$\frac{3}{8}$ -in.-dia. Rod	$2\frac{1}{8}$ -in. \times 0-120-in. Strip	$3\frac{1}{8}$ -in. \times 0-181/ 0-100-in. Commutator Strip
Ultimate tensile strength, tons/in. ²	35.3	32.8	32.8
0.1% Proof stress, tons/in. ²	29.0	29.0	28.0
Elongation, % on 2 in.	14	8	5.5
Brinell Hardness No. (2 mm. ball, 40 kg. load)	148	151	145

Electrical conductivity = 85% I.A.C.S. minimum.

this stage, particularly with material which is to receive a further rolling or drawing pass, batch samples are taken for Brinell hardness and electrical conductivity tests.

3. HEAT-TREATMENT OF COMPLEX ALUMINIUM BRONZES

It is not usually necessary to heat-treat forgings of complex composition generally conforming to D.T.D. 197A and 164A, since the mechanical properties obtainable from these alloys in the as-forged condition usually fall within the limits set in these specifications. It is, however, desirable, and in frequent cases essential, to heat-treat these alloys when produced as rolled or extruded bars and sections. Provided that the aluminium content in the alloy is controlled within fairly close limits—experience revealing that 9 $\frac{1}{4}$ –9 $\frac{3}{4}$ % aluminium is the best compromise—a simple normalizing treatment at 650°–700° C. for 60 min. is sufficient to ensure acceptance under the relevant specifications.

While it may be established that alloys of a higher aluminium content can be used successfully, such alloys are more susceptible to excessive grain growth, unless care is taken to avoid high forging temperatures.

Table V shows the mechanical properties which may be obtained from extruded and extruded and drawn

TABLE V.—*The Effect of Heat-Treatment on Mechanical Properties of Extruded Aluminium Bronze Bar to D.T.D. 197A.*

Composition : Cu 80.34, Al 9.78, Fe 4.93, Ni 4.92, Si 0.013, Mn 0.002%; Pb, Sn, Zn nil.

Treatment	0.1% Proof Stress, tons/in. ²	Ultimate Tensile Strength, tons/in. ²	Elongation, % on 2 in.	Average Brinell No. (2-mm. ball, 120-kg. load)
Specification requirements	25 (min.)	45 (min.)	15 (min.)	179–255
Extruded, 1.025 in. dia.	19.2	50.9	15	209
As above and tempered at :				
500° C. for 30 min.	19.5	49.0	11	218
600° C. " 30 "	20.0	50.5	16	218
700° C. " 30 "	19.5	48.4	21	210
800° C. " 30 "	18.0	49.9	21	206
Extruded, 1.025 in. dia., and quenched from 900° C.	30.6	59.4	2.5	320
As above and tempered at :				
500° C. for 30 min.	36.1	58.6	6	293
500° C. " 60 "	38.3	58.8	5	282
600° C. " 30 "	34.1	56.6	11	263
600° C. " 60 "	31.5	55.4	15	256
700° C. " 30 "	28.5	53.3	18	239
700° C. " 60 "	26.8	51.8	22	238
800° C. " 30 "	23.6	51.0	22	214
800° C. " 60 "	21.1	50.7	23	217
Extruded, 1.025 in. dia., and quenched from 800° C.	14.3	50.4	8	231
As above and tempered at :				
500° C. for 30 min.	20.0	50.5	13	217
600° C. " 30 "	22.7	52.9	21	228
700° C. " 30 "	20.8	49.2	23	207
Extruded, 1.025 in. dia., and drawn to 1 in. dia.	33.4	59.7	8	269
As above and tempered at :				
500° C. for 30 min.	50.2	62.6	7	297
500° C. " 60 "	46.7	61.4	11	295
600° C. " 30 "	41.3	56.9	9	272
600° C. " 60 "	39.5	57.6	14	264
700° C. " 30 "	33.7	53.7	16	242
700° C. " 60 "	31.4	52.2	18	242
800° C. " 30 "	25.0	51.4	23	210
800° C. " 60 "	21.3	50.8	24	206

material complying in composition with the specification D.T.D. 197A. The effects of a variety of heat-treatments are also included.

4. HEAT-TREATMENT FOR THE REMOVAL OF INTERNAL STRESSES

The purposes of this low-temperature heat-treatment are three-fold :

- To avoid season-cracking in alloys susceptible to this phenomenon.
- To avoid distortion of stock during subsequent machining operations.
- To modify mechanical properties.

The alloys most susceptible to failure due to season-cracking are the low-copper brasses (β and $\alpha + \beta$ types) and high-tensile brasses, all normally supplied in the extruded and drawn condition. In addition to this group, rolled and drawn sections of square, rectangular, hexagonal, and more complex profiles, and tubes manufactured in 88 : 10 : 2 gun-metal, the higher-tin (5–10% tin) phosphor bronzes, silicon bronzes, and both leaded and lead-free α -brasses containing less than 85% copper, require a low-temperature stress-relieving treatment before despatch.

It is interesting to note that, on less frequent occasions, failure by season-cracking has been observed in alloys normally considered to be immune. For example, failures have been reported in arsenical copper tubes, aluminium bronze stranded wire, and some low-tin (1–3 $\frac{1}{2}$ % tin) phosphor bronze rolled and drawn sections. Copper tubes produced by the normal production methods employing plug or mandrel drawing will not fail under the mercurous nitrate test, but it is possible to produce arsenical copper tubing which will crack in a corrosive atmosphere if the production programme includes a series of heavy reductions without the use of a supporting plug. These heavy sinking passes produce a stressed condition in the tube—by a mechanism not clearly understood—which is sufficient to cause failure in service. Although examples of this are very rare, it is clearly necessary to avoid such abnormal methods of production in the manufacture of copper alloy tubes. Aluminium bronze strand manufactured from 0.144-in.-dia. wire drawn to about 44 tons/in.² tensile strength or more, and containing approximately 6% aluminium, has been observed to fail by some form of season-cracking when exposed to an atmosphere containing ammonia. However, strand manufactured from wire of a similar composition drawn to a tensile strength less than 44 tons/in.² is immune from failure. It is important to note, therefore, that advantage cannot be taken of the maximum tensile strength obtainable by heavy reductions.

While it is advisable to stress-relieve all bars, rods, and sections in which the susceptible alloys may be produced, it has been observed that the method of manufacture has a considerable effect on the degree of susceptibility to failure by season-cracking. Bars and rods produced by rolling or extrusion followed by one or more reductions in straight lengths on a draw-bench are generally found to be in a highly stressed condition, rendering some form of stress-relief essential.

However, brass and bronze rods, both hexagonal and round in profile, and simple shaped sections small enough in cross-sectional area to be drawn in coil on bull-blocks if followed by a straightening process, do not require heat-treatment.

In all cases where low-temperature heat-treatment is necessary, it is essential that this operation should be completed with the minimum of delay. Examples of failure have arisen on occasions when an unavoidable delay of less than 48 hr. has occurred. In addition to securing speedy treatment, it is essential that pre-treated metal is stocked in a clean, warm, and dry condition. It is advantageous for this reason to instal heat-treatment furnaces adjacent to, and in the same bay as, the plant in which the final drawing operations are performed. If, however, because of plant or space restrictions, this ideal is not possible, and the appropriate heat-treatment plant is in another building, it is desirable to transfer the stock in a covered vehicle.

It is customary to perform stress-relieving operations on copper-base alloys susceptible to failure by season-cracking by a low-temperature heat-treatment in an electrically heated furnace equipped with forced-air circulation. The normal cycle of operations used is 250°–300° C. for 15–30 min., the precise conditions depending upon the alloy and the size and form of the furnace charge. The material should be distributed evenly on the furnace-charging equipment to ensure uniform heat-treatment, and the usual precautions must be taken to achieve accurate temperature control. Routine checks of furnace pyrometers and controlling equipment are necessary, and it is advisable to issue standard data of various heat-treatment cycles for use by the furnace operator.

Low-temperature heat-treatment is frequently employed in the manufacture of most forms of copper alloy products where these are subsequently subjected to machining operations. The relief of internal stress is necessary to avoid distortion, and it is generally accepted that distortion occurs when the internal stress is relieved unevenly as one surface or end of the rolled and drawn bar is removed. This effect is particularly noticeable in the manufacture of engine components such as oil-retainer rings and crank-pin washers from 5% tin bronze in the form of medium-hard-rolled plate. Unrelieved bronze tubing in sizes generally too large in diameter, or too thin in wall-thickness, for reeling will similarly distort to an oval section on sawing to length. The heat-treatment necessary to remove all traces of stress sufficient to cause distortion is generally performed at a higher temperature and for a longer time than that employed for the normal process, to eliminate risk of failure due to season-cracking. It is necessary to heat-treat medium-hard 5% tin bronze rolled plate at 400° C. for 1½ hr. to ensure satisfactory machine-shop production. It must be noted that at this temperature there is some loss of mechanical properties; the Brinell hardness in the example cited falls from 150–180 in the as-rolled condition to 115–125 in the tempered condition.

The modification of mechanical properties in the

example described in the previous paragraph is of secondary importance to the main effect of producing stress-free material which does not distort on machining, but low-temperature heat-treatment is also used to some extent with the express object of modifying mechanical properties to comply with relevant material specifications. It is indeed an art complementary to that of temper-rolling. It is possible to obtain controlled reductions in the ultimate tensile strength and Brinell hardness with a corresponding increase in the values of elongation, and this procedure is now recognized as being necessary for the production of many forms of brass and bronze strip and bar sections where the customer's requirements are of a special nature calling for mechanical properties not easily obtainable by a standard rolling or drawing programme.

III.—FINAL SHAPING PROCESSES

Shearing, straightening, and cutting to length are among the final processes in the manufacture of copper and copper alloy products and, although little or no action can be taken at this stage to rectify material defects which may occur through faulty technique or breakdown of control in the earlier stages of production, it is necessary to introduce certain controls of a general nature to ensure that satisfactory and acceptable products are delivered to the warehouse for despatch to the user.

As the surface finish of most products at this stage has been developed in accordance with the customer's requirements, it is of course essential to ensure that no deterioration of the finish achieved occurs. Care must be taken to avoid damage such as scratches, finger marks, and indentations, frequently the result of careless handling, particularly in the case of sheet and strip manufactured for chemical engraving or for polishing and electroplating. Scratches and heavy score marks usually arise when sheets are allowed to slide over each other, and the number of such defects is considerably reduced by interleaving the sheets with paper. Finger marks can be successfully avoided by the provision of cotton or plasticized fabric gloves for all operatives handling material during the finishing processes.

It is also necessary to take precautions to ensure that material awaiting one or other finishing operation does not become discoloured through attack by the general mill atmosphere. Good general ventilation, particularly in the annealing furnace and pickling bays, lessens this danger, but any metal which cannot be passed through these stages without delay should be temporarily covered with bitumen paper or cloth.

The trimming of sheet and strip by shearing, slitting, and cutting-to-length operations performed on automatic or semi-automatic machines depends primarily for accuracy upon the repetitive capacity of the machine, in addition to the care with which it is initially set up.

Many orders of small weight and non-standard size

are not suitable for finishing on automatic machines. In these cases much depends on the ability of the operator and the care taken to feed the sheet or strip correctly into the shear or saw. This applies particularly to such operations as the cutting of commutator strip into blanks, when an adjustable back-stop or jig is used in conjunction with the cutting-off saw. It is not only necessary to ensure that the back-stop is adjusted correctly, but that it is at all times kept clean and free from sawdust. In addition, it is important that all cutting tools be kept sharp and in good trim by regular toolroom maintenance and overhaul. A simple routine procedure will effectively reduce the quantity of rejections which occur through inaccurate sawing or shearing or through the formation of excessive burrs on the sheared or sawn edge.

The success of rod-straightening and sheet-flattening methods is based on the fundamental prerequisite that the material processed undergoes plastic deformation to an extent which varies according to its condition and to the method adopted. The effect of these finishing operations on the mechanical properties of the material is determined and, where necessary, adequate allowance is made for it in the earlier stages of production to ensure that the material complies with the purchasing specification. When correctly processed, the surface of finished products is smooth and in many cases highly polished. Faulty adjustment of machines can, however, produce a variety of defects, and care is necessary in setting up machines. The conditions necessary for satisfactory production are usually different for each batch of material, and it is generally impossible to lay down a standard code of procedure.

1. SHEARING OF COPPER AND COPPER ALLOY SHEETS

Shearing of sheets is little more than a trimming and squaring of the ends and sides of a blank or strip rolled to dimensions which will produce a standard sheet, suitable for convenient handling and packing and, except in a few cases, the sheared edges are removed in subsequent blanking and forming operations. Permissible tolerances on the length and width of sheets are well within the working capacity of modern plant and, provided that machines are well maintained and operators exercise reasonable care, there should be no difficulty in producing sheets having dimensions within specified tolerances. Cutting shears are usually of the guillotine type, with squaring arms provided at the left- or right-hand side of the machine and a screw-adjusted back-stop for multiple cutting. For medium-gauge sheets it is advisable, and for heavy-gauge sheets it is essential, to use a hold-down while cutting. There are several types of hold-down, that operated by pneumatic cylinders being very satisfactory, as it gives a firm grip on any thickness of sheet without adjustment. In order to avoid damaging the sheet, the hold-down fingers need to be covered with suitable material, vulcanized fibre being commonly used for the purpose.

All shears have a sloping moving blade to reduce the

cutting load, an inclination of about one-in-twenty being common practice. When it is necessary to use the back-stop for cutting narrow strips out of standard sheet or plate, this slope causes the strip to twist as it is cut off, and the distortion must subsequently be removed.

2. SLITTING OF COPPER AND COPPER ALLOY STRIP

For processes where strip in long lengths is required and the tolerance on width and the condition of the edges are not important, or when the strip is too thin to be produced by drawing, it is rolled in coil and the edges are trimmed by slitting. Single narrow widths are rolled if very long continuous lengths are required, such as for the manufacture of flexible tubing or for particular applications in blanking presses, but the bulk of slit strip is produced by multi-slitting from wider coils. Strip for the manufacture of co-axial cable or for use in certain types of blanking operations has to be produced to exceptionally close tolerances on width, necessitating great care in setting up cutters and maintaining the condition of the cutting edges, while the condition of the slit edges is important in strip for the manufacture of gilled tubes for heat-exchangers. Apart from such special applications, the tolerance on width permitted by standard specifications presents no major difficulty to manufacturers.

In general, slitting is a separate operation, although in a few cases strip is edge-trimmed before the final pass, as, for example, when the last rolling pass is very light and it is desired to avoid the slight distortion of the edges caused by cutting relatively soft strip. The cutting assembly can also be arranged between the rolls and coiler drum at the last rolling pass.

There are two main types of slitting machine. In one the cutters are driven, with the coiler winding the strip under slight tension, in which case the speed of slitting remains constant and is controlled by the speed of the cutters; in the second type the winder pulls the strip between the cutters, thereby increasing the speed of winding as the diameter of the coils builds up. For winding up the slit coils, two spindles may be used and the coils wound alternately on them; individual coilers may be provided for each strand, or all the strips may be wound on the same drum with separating plates between adjacent strands. The latter method is particularly suitable when slitting large-diameter coils of narrow strip, as the danger of coils falling over during winding is virtually eliminated and the separators are a considerable help in taking the finished coils from the drum. There is another type of pull-through machine, in which the cutters are run on centres and are made to slit a number of strands of one size only. The profile of the cutting edge is rather like a buttress thread with all the cutting edges pointing the same way on one cutter, with the other cutter in the pair having edges facing in the opposite direction. The clearance is provided by lateral movement of one of the cutter assemblies. This type of machine puts a twist in the strip, and

hence is useful only for material of thin gauges (0.001–0.004 in. thick), where the twist does not result in a permanent set. These cutters cannot be adjusted, the spacing of the cutting edges alone determining the width sheared. Special accuracy in sharpening is therefore necessary, but the machine operator cannot make an error in setting up.

The clearance between the cutters is important in all slitting operations and as a general rule it may be reckoned at 0.001 in. for every 0.008 in. of thickness up to 0.032 in. and 0.001 in. for every 0.010 in. of thickness over. Sharp cutters and accurately set clearances result in good edges free from burr and flat strip of correct width, whereas dull cutters bow the strip across the width and tend to make it run a few thousandths of an inch wide.

The condition of the rolled strip is important in achieving satisfactory slitting. Strip which is slightly longer on the edges than at the centre will edge-trim fairly well, but its flatness will not be improved by taking off the edges; on the other hand, if it is slit the strands will be straight. Strip which is longer in the centre, however, will be flatter after edge-trimming, but after slitting the strands will develop an edgewise bow. Unless the gauge across the width of the strip is constant, the rate of coil build-up with a single-spindle winder will not be the same for all the strands, the thinner ones being relatively loosely wound, and this gives a useful check on the thickness of the strip across the width. It is not possible to make this check on thickness when a multi-spindle winder is used. The centre strands of a slit strip normally tend to run straight, while the outer strands tend to deviate, and although specifications do not usually lay down a tolerance for edgewise deviation from a straight line, the standard aimed at is something less than $\frac{1}{2}$ in. in 6 ft. This side-bias can be avoided only by careful rolling, as it is seldom possible to make any correction after slitting.

The coils are pulled tight while lying on a flat table before binding up with wire, textile tape, or tensional steel strapping, as may be most appropriate to the size and weight of the coils. It is necessary for the coils to be firmly wound and securely tied to prevent damage on the edges during subsequent handling and transport.

Slit material which is required in straight lengths is passed through a roller-flattening machine and sheared to length. In the better type of machine the shear moves with the strip while cutting off, although machines are made in which the feed-rolls stop while cutting off takes place. This is less satisfactory as skid marks may be left on the strip when the rollers start up again after cutting. A fairly thorough routine inspection for surface defects can be made on strip during slitting, and when straight lengths are being produced it may be an advantage to arrange for final inspection to be done by the Inspection Department during the flattening operation. The examiner watches the top surface of the strip as it comes through the machine, and after shearing he turns it over on to a

stack and examines the other side. This saves a handling operation after the material has been transferred to the warehouse.

3. MANUFACTURE OF CIRCLES

If large quantities of one size of circle are required, blanking is the best method of production, and where sets of standard tools are available, small lots are also produced in this way. In addition to certain angles and clearances which may vary with different metals and tempers, the finish of blanking tools is very important, and cutting edges must be maintained in a sharp condition in order to avoid burr and radiusing on the edge of the blanks. For blanking brass and copper discs, the die should be in the hardened condition with an angular clearance of one to five degrees extending to the cutting face or up to a point about $\frac{1}{16}$ in. below this face. The blanking punch, usually left in the soft condition, must be a tight fit within the die for thin material (up to 0.005 in. thick) and a loose fit having an all-round clearance not exceeding 10% of the thickness of the material for thicker blanks. Soft metal requires more clearance than hard metal, and tool wear and quality of edge of blank are controlled by the clearance. Although satisfactory results are achieved without lubricants, tool life is improved by using clean stock with a film of oil spread over the surface before punching.

Circles of medium or large diameter, particularly in the thinner gauges, can also be made by slitting. A square sheet of suitable size is clamped between two revolving centres supported in a bow and swung into the path of the cutters. The setting of the centre of the circling head relative to the axis of the cutters is most important, for if the circle centre is too far in advance, the disc will not be round, and if it is too nearly in line, the edge will be badly burred. With correct setting, however, accurate and well-cut circles can be obtained, the accuracy improving as the ratio of diameter-to-thickness increases.

4. STRAIGHTENING OF COPPER ALLOY WIRES AND RODS

All round material and many plain sections such as rectangles, squares, or hexagons are machine-straightened, whereas complex sections are mostly straightened by hand.

The straightening from coil of wire and rods up to about $\frac{3}{8}$ in. dia. is usually done on spinner-type machines. The stock is fed by grooved rolls into a set of pre-straightening rollers which take out most of the curve from the original coil, then through a second pair of rolls into a rotating frame which carries five adjustable dies set to give the required plastic deformation. The straightened rod or wire passes finally through a third set of feed rolls to a guide-trough, cutting off being done by flying or fixed shear. In the latter case a mechanism is provided to stop the feed rolls while cutting is taking place. A further device is sometimes provided which moves the

spinner slowly backwards while the feed is stopped so as to prevent swelling of the wire. Among a variety of materials used for the spinner dies and the bushes in the end of the spinner are cast-iron, hardened and polished steel, tungsten carbide, bronze, white metal, nylon, Bakelized fabric, hard-wood, and vulcanized fibre. The type of material used depends upon the surface finish required on the straightened wire or rod, but freedom from spiral scratches can be achieved only by using the non-metallic materials.

Rolled and drawn or extruded rods over $\frac{3}{8}$ in. in dia. normally produced in straight lengths are finally straightened on barrel-type reeling machines as described by Smith and Swindells.⁷

Each type of mechanical straightening process may result in an increase of a few thousandths of an inch in the diameter of the material straightened, and it may be necessary to allow for this effect in order to ensure that the finished material is within the tolerances permitted by the customer's specification. During the straightening process the mechanical properties of the wire and rods generally undergo some modification, the extent of the change depending on a variety of factors, including alloy composition, degree of cold work applied, and machine setting. Table VI gives the diameters and mechanical properties before and after straightening of a number of wires of various compositions selected at random from normal production.

If, however, the material is subjected to a low-temperature heat-treatment before straightening, the increase in diameter that occurs during straightening is significantly less—in fact it is generally eliminated. Similarly the mechanical properties of such heat-treated wires suffer little or no change during the straightening process. It may therefore be concluded that the effects shown in Table VI are due to the removal of residual stress present in the wires before straightening.

TABLE VI.—Effect of Straightening on Diameter, Tensile Strength, and Elongation of Wire.

Alloy	Dia., in.		Tensile Strength, tons/in. ²		Elongation, % on 2 in.	
	Before	After	Before	After	Before	After
High-conductivity copper	0.231	0.231	24.0	21.7	8.5	19
70 : 30 Brass	0.249	0.251	31.2	30.9	20	24
62 : 38 " "	0.0638	0.0643	40.8	37.0	4	7
59% Copper, 1.5% lead	0.1755	0.177	41.7	38.8	8	11.5
brass	0.176	0.177	39.5	37.7	7.5	12
5% Tin bronze	0.311	0.3115	36.1	36.0	14	21
" "	0.377	0.378	39.2	37.4	16	20
7% " "	0.080	0.080	64.2	62.0	2	2.5

Roller straighteners with two sets of rollers, one with a vertical and the other with a horizontal axis, and normally provided with flying cutting-off shears, are used for regular non-circular sections. Shaped rollers can be made to suit special sections and are used where the quantity to be straightened is large enough to justify the cost of new rollers.

The more irregular sections, extruded sections in particular, are commonly straightened by hand, no machine method being sufficiently adaptable. For sections that can be suitably gripped a stretching machine may be used, twist being removed by a rotating grip at one end or by wringing irons applied by hand according to the size of the section.

It is unfortunate that, in spite of the advent of considerable mechanization, straightening is still an art. The operator must have a natural aptitude for the process if success is to be achieved. This particularly applies to those sections of irregular profile which can be straightened only by hand. Variations of stress and distortion are infinite, and no set rules can be applied or common practice adopted. Even with mechanical straightening, where the stock is of regular profile, an experienced operator may find it necessary to make several adjustments to rollers or dies before satisfactorily straightened material can be produced.

The normal finishing operations employed in the manufacture of certain copper alloy rods and sections frequently set up internal-stress gradients which may cause failure owing to season-cracking under certain conditions of storage or service. As discussed earlier, alloys susceptible to this type of breakdown are normally given a low-temperature stress-relieving treatment. It is of interest to note, however, that it is possible to stress-relieve some of these alloys in the cold-rolled or drawn condition by mechanical means. Phosphor bronze rods and sections drawn in coil and subsequently straightened by one or other of the available mechanical processes appear to be immune from risk of failure in service and withstand the mercurous nitrate test without low-temperature heat-treatment. This mechanical stress-relieving process is not, however, reliable in the production of wrought 88 : 10 : 2 gun-metal in any form or of phosphor bronze and brasses which have been finished by one or more passes on a drawbench.

5. STRAIGHTENING, CUTTING TO LENGTH, AND DEBURRING OF DRAWN COPPER BARS AND SECTIONS

Methods of straightening copper bars and sections are very similar to those used for straightening copper alloy bars and sections, but greater care is necessary to avoid damage to the surface owing to the fact that copper, even in the hard-drawn condition, is softer than most of the copper alloys. When drawing bars of large cross-sectional area (e.g. $6 \times \frac{1}{2}$ in., and larger) and also smaller-section commutator bars, it is necessary to give great attention to drafting, positioning of the drawing die, and guiding of the material into the die, as straightening is a difficult operation by the usual method of hand malleting. As the quantities do not often justify expenditure on a bar-straightening or stretching machine, improvisation is usually made by supporting the bar at two points and pushing against the bend with a screw or hydraulic ram. Alternatively the bar may be tempered to such

a degree that it will straighten by malleting, but only at the expense of some loss of mechanical properties. Commutator bars about 1 in. wide and over are straightened by hand, by stretching, or by placing two bars together to form a rhomboidal section and passing them through a roller straightener; if the latter method is used, however, it is still necessary to hand-straighten on edge.

Benches with fixed-table saws are in common use for end-trimming, and when exact lengths to normal commercial tolerances are required, adjustable stops are fitted to the benches. Alternatively, the bars may be clamped for sawing with cross-feed or pendulum-type saws, a satisfactory method if short lengths are required. An adjustable table is used if commutator bars are being sawn to shape ready for assembly, and the table is set at an angle to the horizontal equal to half the included angle of the commutator bar so that the brush-bearing surface makes equal angles with the faces of the bar.

The removal of burrs from sawn bars can be effected by hand filing, rubbing on abrasive wheels, or tumbling with or without abrasive chips. If considerable quantities of bars are to be deburred hand-filing is too slow, and it is more usual to remove the burrs by means of an abrasive wheel. Tumbling is used only for short pieces, and unless the burrs are slight it is necessary to use some form of abrasive chip, with the attendant disadvantage of having to separate the chips from the metal pieces after tumbling. The method is not entirely satisfactory for copper components, since excessive abrasion frequently occurs at the corners, and if the burrs are large there is a tendency for them to be pushed over rather than to be completely removed.

6. STRAIGHTENING, CUTTING TO LENGTH, AND DEBURRING OF TUBES

The degree of straightening necessary for tubes depends on the condition in which they come from the finishing benches, and therefore by careful control at the final pass the time for straightening is reduced and the quality of the tubes is improved. Some of the points to be observed at the final drawing stage are: (i) true alignment of the die-bearing surface with the machine, simplified on modern drawbenches by having adjustment screws in the die box; (ii) adequate support of the tube to give a straight lead into the die, especially where annealed tubes are being given a light pass; (iii) a good supply of lubricant all round the die. If they are not properly supported at the back of the die, there is a tendency for the tubes to be irregularly distorted, while eccentric tubes tend to finish with a constant bow or curvature. Hand-straightening is still employed, particularly on small lots, but whenever big batches of a size are available, machine-straightening is preferred. The most common type of straightening machine is the high-speed tube-straightener with two driven, and three or more idle, rolls, although there are machines with six horizontal and six vertical rolls. For large-diameter or thick-

walled tubes, barrel-type reeling machines may be used. The high-speed straightening machines are in no sense automatic and a certain amount of skill is required on the part of the operator. It is important to watch the condition of the rolls and bottom steady, otherwise tubes are readily marked. There is a slight increase in the diameter of tubes after passing through the straightener, and an allowance on the die size of 0.001 in. is made for tubes up to 1½ in. dia. A corresponding decrease in length results, and therefore if close tolerances on length are specified, cutting to length must be done after straightening. Excessive pinch on the rolls causes spiral grooves, giving high and low dimensions on diameter. When setting up the machine it must be remembered that a tube acquires some degree of work-hardening while passing between the rolls, and therefore should be passed through once only in the first batch trial. If, after the machine has been set up, an occasional tube is not properly straightened, no attempt should be made to adjust the machine. The few tubes thus accumulated can receive special treatment after the main batch has been straightened. If tubes are badly distorted, some hand-straightening may be necessary before passing through the machine.

Sawing is usually done by either lever-type and cross-feed saws or fixed-table saws, the latter type being more commonly used in this country. It is claimed that the lever-type or cross-feed saw results in cutting more squarely with less effort on the part of the operator, but sliding guides can be attached to fixed-table saws, and if these are not used the operator must see that the tubes travel at right angles to the saw blade to ensure square ends. Distorted ends can result from exerting too much pressure when feeding to the saw, especially with thin-walled or soft tubes. Fine-toothed high-speed saws are satisfactory, and good maintenance and frequent changing reduce the amount of burr on sawn ends. Slow-speed segmental-saws with automatic feed and vices or clamps for gripping the tube are more suitable for large-diameter and thick-walled tubes, and if square ends to a very close tolerance are necessary on large tubes, it may be necessary to machine the ends.

Removal of burr is done by cone-headed reamers, scraping blades, or wire brushes, all of which can be mounted directly on the spindle of a low-horse-power, high-speed motor. Reamers or scraping blades usually produce a radiused or chamfered edge. Wire brushes are more efficient and produce a smooth burnished edge, but there is a tendency for heavy burrs to be pushed over and not removed.

IV.—INSPECTION

1. GENERAL

The final control on material before passing on to the warehouse for packing and despatch is made by the Inspection Department. In organizations whose concern is with the manufacture of non-ferrous metal

intermediates, it is normally regarded as advisable that the Inspection Department should not be under the control of the Production Management. The department should not be looked upon as being responsible only for acceptance or rejection of material, for it can make a very important contribution to the maintenance of quality throughout the factory. Records of inspection should be kept in reasonable detail, and where material is made by a standard method of production, full inspection reports should be made giving reasons for rejection and percentage of material rejected, with a summarized report issued less frequently detailing the rejections for each section. Such reports are essential for good management and efficient costing, and, in addition, they will provide information which can be used in drawing up specifications and for dealing with specifications which demand properties or tolerances closer than those which are normally considered as standard. In flow-line production, inspection benches for surface examination, gauging, selection of test-pieces, hardness testing, or pressure testing can be arranged in the flow-line between the finishing operation and the warehouse. For small lots of various shapes and sizes, final inspection is usually carried out after delivery to the warehouse, although in some instances it may be more convenient to do part of the inspection in a finishing department adjacent to a saw or shear. It is difficult to examine for surface defects long lengths of material in coil and on drums, such as strip and trolley wire, and in these cases arrangement is made for inspection during the course of the final drawing or rolling operations.

The procedure for inspection is usually laid down in British Standards or other specifications, and if material is not ordered to a specification, the relevant British Standards may be used as a basis for inspection. The number of tests taken in relation to the quantity or number of pieces in a batch varies considerably, and may be less than 1% for some mechanical tests and as high as 100% for hardness, hydraulic, and other tests.

2. CHEMICAL COMPOSITION

With modern methods of chemical analysis, control of composition is introduced at the casting stage, and it is now common practice to take samples for chemical analysis from each furnace charge before castings are released for further processing. In addition to this it may also be necessary from time to time to make analytical checks on samples taken from finished material as a specification may demand this procedure. The chemical test may also be used as a check where irregularities are encountered in mechanical, electrical, or other tests, e.g. variation in colour of fractured test-pieces. Often a quick, qualitative physico-chemical test can be used for sorting where different qualities of material are mixed within the same batch. Care must be exercised in the sampling of metals for analysis and B.S. 1499 has been drawn up to cover the sampling of non-ferrous metals.

3. SURFACE QUALITY AND INTERNAL DEFECTS

Most specifications include a clause calling for material to be clean, smooth, sound, and free from surface and other defects. Since these are all relative terms, examination can only be arbitrary, and strict adherence to the letter of a specification would ordinarily demand a very high standard of quality quite regardless of the end-use of the material. As a result of experience and some knowledge of customer's requirements, standards of quality can be agreed and used as a basis for acceptance or rejection, and if an examiner finds any failure to maintain any such standard, the matter should be reported to those responsible for manufacture. In spite of careful surface examination, certain types of defect, such as those arising from rolling fins in rod or wire and blisters on sheet or strip, may not be noticed by the examiner, and a simple form of test is usually devised to find them. By twisting and de-twisting a rod or wire in a standard type of torsion-testing machine, fins are more readily observed (Fig. 3, Plate XXXIII), and when a batch of material is in doubt a sample from each coil can be subjected to the test; the twisting test can be usefully applied at the last rolling stage before drawing. The effect of the set side of a wire-bar in drawn wire is also revealed by this test. Defects arising from rolling fins are to be avoided in any type of material which is subjected to a heading operation or in wire which is subjected to vibrational stresses in service and is liable to early failure by fatigue (e.g. line wire, aeriels, and trolley wire) and the twisting and de-twisting test can be used for sorting out faulty material.

Sub-surface defects occasionally occur in sheet and strip as a result of the presence of gas pockets or shrinkage cavities in the casting. Such defects, which may be detected in annealed strip of thin gauge as blisters on the surface, are not usually visible in hard-rolled material. In the absence of a reliable non-destructive method of testing for this type of unsoundness, a simple bend test (Fig. 4, Plate XXXIII) is normally employed.

Fracture tests are made on strip, rod, or wire to reveal internal defects which arise on occasion during the casting or extrusion process, and a specification may demand 100% fracture. The test is applied by nicking and breaking, since a shear cut may cover a fault (Figs. 5 and 6, Plate XXXIII), or on the other hand a chip in the shear blade can give an apparent fault. If this test is used it is better to make the cut at an angle of about 45° and not at right angles to the longitudinal axis of the material being tested. Certain types of internal defects, such as oxide inclusions in aluminium bronze or even very slight piping, are not readily shown up by fracture tests, and in such cases it may be necessary to section and polish a specimen for examination at a low magnification. An unusual type of internal defect is the cuppy or broken centre peculiar to certain types of copper alloy when subjected to an extreme amount of cold work. The

centre of the rod is fractured at regular intervals in the form of an almost perfect cup and cone, and if drawing is carried on considerably beyond the stage when fracture first takes place, defective material can be detected by waviness on the surface of the rod. When drawing has not gone sufficiently far to cause waviness, there is a danger that the fault may not be detected when sawing to length, as shown in Fig. 7 (Plate XXXIII).

4. DIMENSIONS AND TOLERANCES

Tolerances on dimensions are included in practically all specifications, and to check the diameter of wire or rod or width and thickness of strip or sheet, direct measurement is made by hand micrometers or, alternatively, "go" and "no-go" gauges may be used, the latter method often being applied when it is necessary to make 100% inspection on one dimension. It is important that all measuring instruments be checked periodically against master gauges.

Difficulties often arise when checking the dimensions of fine wire and thin strip, where tolerances may be of the order of 0.0001 in., and with hand micrometers errors arising from pressure on the micrometer screw, ovality of wire, or the human element may be greater than the specified tolerance. A dimension can be calculated, provided that the density is known with sufficient accuracy, from the weight per unit length of wire or strip, but this does not provide a measure of ovality when checking wire diameter or variation across the width of strip when determining thickness by this method. There does seem to be a real need for a suitable instrument for checking these fine dimensions. Tolerances on length of material ordered in straight lengths are generally wide enough to permit checking by rule or tape, and only when a very close tolerance on length is specified should it be necessary to take special precautions. When checking to a close tolerance, errors can arise from factors such as bent rod or strip (particularly if the material is in the soft condition), temperature variation, or flexibility of the rule or tape. Dispute sometimes arises between supplier and customer on the question of flatness or squareness, owing to the fact that no tolerance is permissible in some specifications for bars and tubes if the specification is taken literally. It is not unusual for a specification to state "... and the ends shall be cut square", which is in effect equivalent to specifying $90^\circ \pm 0.000^\circ$. An agreed tolerance on squareness for British Standards would be welcomed by manufacturers, for although on long random lengths the question of squareness may never arise, when shorter lengths cut ready for assembly are ordered, it may be very necessary for the bars to be sawn to close tolerances. A case in point is furnished by commutator bars cut to length for assembly on end.

5. MECHANICAL TESTS

It is not intended to describe in detail the machines used for making the various mechanical tests or the

method of carrying out the tests, and reference should be made to British Standard Handbook No. 13, which brings together all methods of mechanical testing established in British Standards. This book deals with the subject in ten sections as follows:

1. Tensile Tests.
2. Hardness Tests.
3. Impact Tests.
4. Ductility Tests.
5. Tests on Thin Material.
6. Creep Tests.
7. Verification of Testing Machines.
8. Transverse Test.
9. Miscellaneous Tests.
10. Conversion Factors.

Frequent checks should be made on the accuracy of all testing machines and apparatus, using calibrated specimens generally supplied by the machine makers.

When mechanical tests are made, in addition to a record of a value for hardness or breaking load, careful examination should be made of the type of fracture or indentation, the surface of the distorted test-piece, and the colour of the newly made fracture, as such observations provide evidence of a breakdown in the control of quality during some stage of manufacture. Even when tests are within specification requirements, the surface condition of a broken test-piece may indicate that annealing has been carried out at too high a temperature, a fracture may reveal inclusions and internal defects, or the colour of fractured test-pieces may indicate some variation in composition, and a warning can be passed to the Production Department.

6. ELECTRICAL TESTS

Copper and copper-base alloys used for electrical purposes, such as copper or copper-cadmium alloy power cables, trolley wire, and telegraph and telephone lines, strip for bus-bar installations, taper and other sections for commutator bars, small rectangular sections for transformer windings or windings for rotating electrical machinery and sections for rotor bars, are all subjected to an electrical-resistivity test. The resistance is usually determined by direct measurement on wire or strip, or on wire drawn from sheet or strip. The effect of small amounts of impurities on the electrical properties of copper and copper alloys is well known, and if there is a doubt about the quality of a batch of material, the electrical-resistivity test is a valuable non-destructive method for sorting. There are instances where the test has been used to check the amount of an impurity or added element in copper, such as the amount of phosphorus in a low-phosphorus-bearing copper, but the effect of small amounts of other impurities must not be overlooked, and correction must also be made for any variation in cross-sectional area. If this method is to be used as an acceptance test, as for instance when numbers of pieces have to be examined, frequent checking by chemical analysis should be carried out.

7. HYDRAULIC TESTS

Tubes required for water and air services are subjected to a pressure test, usually applied to each tube, and they must withstand this test without showing signs of weeping, leaking, or permanent increase in diameter. Failure to withstand the pressure test is generally due to small pieces of foreign matter becoming embedded in the walls of the tube or to scale marks and indentations developing into small holes as the thickness of the wall is reduced by successive drawing operations. Very often a folded tube not detected by visual examination will be found by the pressure test (Fig. 8, Plate XXXIII). The fold, which may result from hollow sinking a dented tube, opens under the pressure test, with a resultant increase in diameter. Precautions are taken in tube mills to avoid damage to tubes and pick-up of foreign matter, and modern preheating furnaces with controlled atmospheres give tube shells which are free from scale marks and embedded scale, with the result that the hydraulic testing benches run for long periods without finding a leaking tube; in fact, rejections for these reasons never exceed a small fraction of 1% of the total number of tubes tested. General practice in America is to select a number of lengths equivalent to 0.2% of the batch for pressure testing. A pneumatic test by which the tubes are subjected to air pressure whilst submerged in water is an alternative method in many American Standards, and is beginning to find favour in this country. B.S. 2017 permits the test as an alternative to the standard hydraulic test, but only by arrangement between the purchaser and the manufacturer.

8. MERCUROUS NITRATE TEST

This is a test for detecting the presence of residual internal stresses in many copper-base alloys. The method is described in an appendix to B.S. 378 (1953), and in A.S.T.M. Designation: B154-51.

9. GRAIN-SIZE DETERMINATION

It is essential with certain types of copper and copper alloys—particularly those which are composed entirely or substantially of the α -phase and which are subjected to deep-stamping, polishing, or plating operations—that the grain-size shall be controlled within specified limits. The strained surface on a cupping, bend, or tensile-test specimen may be used as a good qualitative test on material intended for such operations, and methods for estimating the average grain-size of wrought copper and copper-base alloys are given in detail in A.S.T.M. Designation: E79-49T.

10. SPECIAL TESTS

There are occasions when none of the accepted standard tests will prove that a material is suitable for a particular application, and often after consultation with a customer a form of test can be devised to simulate subsequent working operations on the

material. Typical examples are an edgewise bend-test for material bent or coiled on edge; a machining test, where the stock is subjected to a turning, drilling, or screwing operation; a heading or flattening test on wire or rod used for the manufacture of rivets, screws, or bolts; measurement of the permanent set developed in copper alloy wire after the application of a standard strain; or the measurement of elastic limit of brass wire for the manufacture of Fourdrinier wire cloth.

V.—PACKAGING AND DESPATCH

It is the responsibility of the Warehouse and Transport Departments of any manufacturing organization to ensure that the product received is delivered promptly to the correct destination in the same condition as it left the manufacturing department. To achieve this it is necessary to consider: (a) the location of the warehouse in relation to the producing departments, and (b) the type or method of packing to ensure safe transit to the customer.

It is essential that all unnecessary handling and movement of finished material, especially in the soft or semi-hard state, be avoided. For this reason, apart from considerations of efficiency, the warehouse is normally sited at, or near to, the end of the production line. The building should be warm, dry, and well ventilated to prevent staining and corrosion through condensation of moisture on the exposed surfaces of material awaiting packing. These conditions, together with the presence of quantities of packing materials such as straw and wood wool, will unfortunately attract pests such as birds and mice. Both creatures can cause damage to the surface of finished products in store, and it may be necessary to adopt methods of eradicating them.

The method of transfer of material to the warehouse depends chiefly on its form and condition. Hot-rolled copper and copper alloy strip and rods in coil are normally conveyed by crane or fork-lift truck, and no special precautions are taken to avoid damage. Rolled and drawn wire, rods, and strip of hard temper are transferred in a similar way, employing soft copper-strand or manila-rope crane-slings to avoid surface abrasions. Soft copper wire, annealed copper, and copper alloy sheets and strip, and particularly foil and soft copper strip with rounded edges are usually loaded into pallets or other suitable forms of container. Use is made at this stage of a variety of materials, such as softwood, felt, or corrugated paper, as spacers to separate adjacent coils or sheets. This precaution eliminates the risk of indentations and abrasions caused through the relative movement of adjacent metal surfaces.

The final inspection of orders ready for packing and despatch is frequently carried out in the warehouse, thus reducing the risk of mechanical damage after release by the inspecting authority. Provision should be made on the order card, which accompanies the material through the producing departments to the

warehouse, for the inspecting official's signature; this indicates that the material has been inspected and approved, and is the final authority for despatch. This procedure is additional to the special arrangements that operate during the inspection and release of material for Government and certain other orders and contracts.

The type of packaging employed for the safe conveyance of copper and copper alloy products varies according to the form and temper of the material ordered, the probable mode of transport, and the climatic conditions to be expected in transit. Frequently the customer will specify the type of packing, but more generally previous experience of successful or unsuccessful deliveries provides a fund of information upon which decisions are made by the warehouse staff. In all cases, however, and particularly in case of doubt, reference should be made to the excellent British Standard Packaging Code (B.S. 1133).

As far as the non-ferrous industry is concerned, the packing of most products is done in cases or on drums or reels. Cases are made principally from softwoods. During the Second World War the industry was obliged to use much unseasoned home-grown hardwood, most of which had an adverse chemical action on copper and its alloys. However, one or two of the imported hardwoods were found to possess most of the merits of softwood, and were stronger and rarely warped. For instance, Agba, which weighs only 30 lb./ft.³, is easy to work and nail, has strength properties similar to those of Central American mahogany, and is very resistant to decay. Another useful hardwood is Obeche, the density of which is only 24 lb./ft.³.

The use of specially treated softwood gives a considerably longer life to cases used for the home trade. Experience has shown that at least 40% more journeys can be made with cases constructed of timber impregnated by a proprietary process employing a mixture of copper sulphate and chromate.

All cases, drums, and reels must be carefully examined before being put into service, particularly if they have been previously used. It is important to remove from service any that show sign of serious mechanical damage, dry or wet rot, or attack by fungus, which could cause corrosion, discoloration, or even a complete collapse of the case with serious and costly damage to the contents. As far as possible, cases and drums should be stored in warm, dry conditions. Much damage to case and contents frequently occurs when case-lids and drum-laggings are nailed into position. This method is strongly deprecated. The use of tensional-steel strapping-tapes eliminates this risk entirely. In addition, it reinforces the case and affords economy in materials, while the risk of pilferage is reduced.

Highly polished sheets and circles are usually interleaved with acid-free tissue paper and carefully packed in cases lined with waterproof paper. Straw and wood wool are used extensively to prevent movement.

Coils of copper and copper alloy strip of thickness less than 28 S.W.G. are usually "floated" in special containers on wooden or steel bearers according to the eye-diameter of the coils. Each coil may be separated from the others by either cardboard or good-quality felt pads. Felt of inferior quality may contain small particles hard enough to damage the strip in transit.

Careful selection of suitable packing materials has overcome many problems of corrosion and water-staining of copper products occurring during delivery to the user. This is particularly evident in the case of export orders, which may experience extremes of climatic conditions *en route*. Such modern packing papers as polythene- and wax-coated Kraft, bituminized crêpe, Kraft-faced corrugated boards, and their like are now used extensively. Corrugated paper having a pure Kraft face obviates any chemical action which might develop with the use of ordinary corrugated paper.

The use of hessian as a wrapping material for coils of wire and strip for home trade deliveries has been largely superseded by bitumen and plain crêpe papers. Wrapped closely and tightly on a wrapping machine, they are at least as good as hessian, which allows grit to penetrate through and quickly absorbs water unless suitably treated. Hessian wrappings are, however, still used extensively for export orders of hard wire, above 20 S.W.G., bars and rods, to conform with the requirements of the customer's specification.

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REFERENCES

1. W. W. Kee, *J. Inst. Metals*, 1953-54, **82**, 316.
2. W. C. F. Hessenberg and E. C. Mantle, "Bright Annealing of Copper and Its Alloys" (*B.N.F.M.R.A. Development Report No. 50*). 1947: London (British Non-Ferrous Metals Research Association).
3. H. S. Campbell, *J. Inst. Metals*, 1950, **77**, 345.
4. W. O. Alexander, *ibid.*, 1939, **44**, 104.
5. G. V. Raynor, *Inst. Metals, Annotated Equilibrium Diagram Series*, 1949, (7).
6. — "Beryllium Copper Alloys", 1949: Radlett, Herts. (Copper Development Association).
C. Smith and N. Swindells, *J. Inst. Metals*, 1953-54, **82**, 332.

THE PRODUCTION OF LIGHT-ALLOY DROP-FORGINGS, THEIR HEAT-TREATMENT, INSPECTION, AND TESTING*

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SYNOPSIS

The importance of close liaison between the designer and the manufacturer of drop-forgings is emphasized. A detailed comparison is made between the different types of aluminium alloy forging stock with respect to their forgeability and the quality of the resultant forgings. The significance of the various factors involved in the heat-treatment of aluminium alloy forgings is discussed.

Methods of inspection and types of defects commonly found are described. The relationship between macrostructure, microstructure, and mechanical properties of forgings is considered.

Examples are also given of present-day magnesium alloy forging practice.

I.—INTRODUCTION

DEVELOPMENTS in the aircraft industry over the past few years have led to the adoption of certain new procedures within the drop-forging industry. The dimensional tolerances for forgings have become smaller, and users have come to demand that the strength and other metallurgical features of forgings should be accurately known. Close liaison now exists between the designer and the forging manufacturer from the drawing-board stage. During recent years, specifications have been introduced which necessitate a full metallurgical investigation into every type of forging. This has resulted in forgings no longer being accepted only on the basis of alloy composition and physical properties derived from standard test-pieces; certain agreed properties in the forgings must also be attained, and conditions have been laid down whereby the properties of forgings must be determined at stated intervals during any production run. These requirements have resulted in raising the standards of dimensional accuracy, surface finish, and other general features.

To meet these requirements, new conceptions of production techniques and control have arisen in the drop-forging industry. Before a drawing or design has reached the final stage, it is now usual for discussions to take place between the aircraft manufacturer and the forger to settle questions of grain flow, mechanical properties, and other problems associated with the production of forgings. The hot forging of aluminium and magnesium alloys has been very well described by Stokeld¹ and by Wilkinson and Fox.² The present paper describes in some detail the salient

features of current drop-forging practice, particularly in relation to quality control.

II.—DIE DESIGN

The production of a drop-forging in closed dies necessitates the cutting of an impression in two blocks of steel, referred to as "dies"; the impression in the blocks or dies corresponds to the surface contour required for the two halves of the forging. The junction of the two dies, called the "parting line", is determined by the general symmetry of the forging. The parting line is of further importance in that, where there are several possibilities of parting, the actual line is decided by metallurgical considerations such as continuity of grain flow and the strength required.

At a short distance from the impression, a recess or gutter is sunk to provide an outlet for excess metal—the "flash"—which is subsequently removed by trimming tools in presses or by band sawing.

The die faces are usually flat, but certain forgings can be made only by "stepping" the faces, i.e. inclining the die faces at an angle; wherever possible, however, stepping is avoided on grounds of economy in die-sinking and ease of production. The impression is cut by the usual methods of shaping, milling, &c., and is finally finished and polished by hand. This final polishing is important because on it depends the surface quality of the forging and also to a large extent, the life of the die. The dies are made in nickel-chromium-molybdenum steel No. 5 (British Standard No. 224) and are usually cut or sunk in the hardened and tempered condition so as to avoid distortion during heat-treatment.

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Die life depends on the design of the forging being made. Some dies can provide up to 2000 forgings, but where the design involves sharp radii, unevenness in section, deep lugs, or bosses, runs will be very much shorter as a result of early erosion and cracking of the dies. When dies become unserviceable from these causes, it is necessary to take a machining cut over the die faces and to extend the depth of sinking from the new faces. The die life, metal flow, and forging surfaces are improved by the use of suitable lubricants. Various proprietary brands are available, consisting of oil or spirit impregnated with graphite. Petroleum jelly impregnated with graphite is also used. The choice of lubricant is influenced by the die design and speed of working.

III.—THE FORGING PROCESS AND FORGING DESIGN

The forging process is a means of producing intricate metal shapes with mechanical properties superior to those obtained from castings. The process is carried out at a suitable temperature; for aluminium alloys the range is 360°–480° C., the actual temperature being dependent on the particular alloy.

There is comparatively little movement of metal in the forging die. For normal forgings, the "use" or "dummy" approximates in length and width to the die impression, and movement really consists of the displacement of material into the bosses and lugs, any excess being forced into the flash. The drop-forgers' art manifests itself in the preparation of the dummy by hand- or free-forging methods, so that the work done in the dies is reduced to a minimum. Where the design is such that this is not possible, preparatory dies are used, which are very much oversize in relation to the finishing dies. This preparatory shaping in dies, apart from greatly assisting correct metal flow, also relieves the final dies of much work and wear.

The relation between dummy weight and hammer weight must be carefully considered. It is essential that the hammer be heavy enough to move the metal readily. A hammer of insufficient weight can lead to premature die failure, and also to the production of an unsatisfactory forging, because continued hammering and die movement are a cause of folds, &c., in the surface of the forging. A wide range of hammers is in use, weighing from below 10 cwt. up to 20 tons.

The forging procedure adopted in any given case must take into account the properties required in the forging, and the metal must be prepared and laid in the dies in such a way that the correct grain flow is achieved in the final forging.

In designing forgings it is necessary, from the point of view of metal flow or displacement, that all radii shall be as large as possible. Forgings having small radii need a large number of blows and the use or dummy may have to be reheated several times before it completely fills the dies. Prolonged hammering over a range of temperatures (as the metal in the dies

is cooling off) causes laps or folds during forging; moreover, if the radius is adjacent to the flash line—which can be regarded as the metal-escape route—flash-line cracking may occur. To demonstrate this point, a die was sunk having three ribs with a different radius ($\frac{1}{4}$, $\frac{1}{2}$, or $\frac{3}{4}$ in.) at the base of each, and forgings were made in two alloys, L.65 and D.T.D.683, and at three different temperatures, namely 400°, 440°, and 480° C. The forging was reheated twice at the stated temperatures during the operation. Fig. 1 (Plate XXXIV) shows a partly made and a completed forging. Macro- and micro-sections were taken from the forgings and examined at the radii. The findings can be summarized as follows:

(1) Folds and flash-line cracks occurred most readily at the base of the rib with the $\frac{1}{4}$ -in. radius.

(2) Flash-line cracking was minimized if the surplus metal at the centre of the forging, as well as the flash, was removed before the final heat. (The flash formed was removed before each reheat at temperature.) This enabled metal to move inwards as well as outwards.

(3) Susceptibility to flash-line cracking increased with temperature, and in both alloys local overheating was found at the $\frac{1}{4}$ -in. radius, close to the flash-line cracks in forgings made at 480° C.

(4) An excessive number of finishing blows at a high temperature encourages flash cracking. Such cracks occurred across the base of the rib with a $\frac{1}{2}$ -in. radius after five heavy finishing blows at 480° C., but not if only two blows were given.

(5) No defects were produced under any conditions in the $\frac{3}{4}$ -in. radius.

(6) Cracks formed at the $\frac{1}{4}$ -in. radius at a minimum temperature of 440° C. for the L.65 forging and of 400° C. for the D.T.D.683 forging. There was no notable difference between the alloys at the $\frac{1}{2}$ - and $\frac{3}{4}$ -in. radii.

Fig. 2 (Plate XXXIV) shows a macro-section across $\frac{1}{4}$ - and $\frac{3}{4}$ -in. radii in a D.T.D.683 forging made at 440° C. There are no defects at the $\frac{3}{4}$ -in. radius, but the ribs with the $\frac{1}{4}$ -in. radius have been completely sheared from the web of the forging. Fig. 6 (Plate XXXV) shows local overheating close to a flash-line crack in an L.65 forging made at 480° C.

Another particular aspect of forging design is that involving the use of the "stepped" dies already mentioned. In cases where the grain flow is required to turn through 90° or more, as indicated by the arrows on the forging in Fig. 3 (Plate XXXIV), the dies are sunk in the manner shown in Fig. 4 (Plate XXXIV), the top die being the plain-faced one. The bottom die is sunk with a free space. In addition, by "stepping" or "pitching" the die faces, an angle of turn of more than 90° becomes possible, because the forging, after making, can be pushed or lifted off the die impression. The use or dummy is laid on the bottom die and, in this instance, one of the effects of the blow from the top die is to turn the bar, and hence the grain-flow direction, through 112°. This is one of the cases mentioned earlier where "stepped" dies are necessary

to provide the designer with the continuous grain flow he needs in the forging.

Ring-type forgings provide a good example of the use of pre-forging and die-forging techniques to ensure a continuous circumferential grain flow. The metal to be forged is flattened to a circular disc and a hole is bored through the centre. The disc is then placed on a mandrel and forged down to the required diameter. The effect of this method of forging is to produce a grain flow which extends completely round the circumference of the ring. This ring can then be placed in dies and forged to produce the surface contours.

The forging design and die design having been settled, the production of a good forging depends upon the choice of stock and the initial preparation of the dummy before placing in the dies.

IV.—CHOICE OF FORGING STOCK

The raw material for making aluminium alloy drop-forgings may be extruded, cast, rolled, or pressed. In all cases it is desirable that the original casting should have been produced by the continuous-casting process.

Each type of stock has certain advantages and disadvantages as far as the forger is concerned. In this country most aluminium alloy drop-forgings are made from extruded bar, but there are certain applications for which the use of rolled, pressed, or cast material is advantageous. A detailed comparison of the alternative types of stock is given below.

1. EXTRUDED STOCK

This type of material is generally easy to forge and has a fibrous and largely un-recrystallized structure which may be utilized to provide good grain flow in the forgings, with maximum strength and ductility in a longitudinal direction. The surface quality of extruded bar is usually good, thus facilitating the production of forgings free from surface defects.

Extruded bar may possess certain defects or other undesirable features which are not readily detected by normal methods of inspection. Double-skin, for instance, is revealed only by macro-examination of the bar, unless blistering appears on the surface. If present, it will almost certainly give rise to blistering on the forgings when they are heat-treated and will probably result in their rejection.

Another type of defect occasionally encountered in extruded bar is due to overheating during extrusion. In some cases, this is not severe enough to impair forgeability, and the small amounts of liquated eutectic may be so broken up in forging that their effect on the mechanical properties is negligible.

It is not intended to convey the impression that more than a very small proportion of extruded forging bar suffers from overheating, but merely to point out that it is possible for such a defect to escape detection before the material is used by the forger. It has been found that overheating during extrusion is not

necessarily confined to areas near the surface, but may extend throughout the cross-section of a bar of substantial size. Even when overheating takes place only near the surface, upsetting—which sets up considerable tensile stresses at the surface—is liable to result in a series of bursts. Evidence of overheating has been found in extruded bar to specifications D.T.D.683, D.T.D.364, and D.T.D.731.

By far the most troublesome aspect of the use of extruded bar for forging is that a proportion of it is susceptible to the formation of large grain, especially in the case of the Duralumin-type alloys. Large-grain structures are undesirable because they have much lower tensile properties than fine-grain structures. Much has already been written about this subject, and numerous attempts have been made to solve the problem of large grain, but no economical and thoroughly practicable method has yet been evolved. The reasons for the formation of large grain are well known and, in general, only the back portion of an extrusion is susceptible to it.

Recrystallization to give large grains occasionally occurs during preheating for forging, and this may or may not cause trouble during the forging operation, depending on the procedure adopted. If large grain appears in preheating bar for upsetting, an objectionable “orange-peel” effect will be produced on working the bar. If, after flattening, the discs are forged in closed dies, as in the manufacture of impeller forgings, the irregularities around the perimeter are closed up in such a way that a network of small folds containing oxide is produced. These folds may be up to $\frac{1}{4}$ in. deep. Even if such defects are of insufficient depth to cause rejection of a forging, they give it an unsightly appearance and cause extra work, since part-machining may be necessary to remove them before the forging can pass inspection.

In recent years it has become the general practice to produce small sizes of forging bar by extruding from a large-diameter billet, using a multi-hole die. In this way bars of diameters up to about 3 in. may be extruded, in as many as seven lengths at a time. From the extruder's point of view, this is an ideal method of producing large amounts of bar very economically, but it is not always so satisfactory from the forger's point of view.

Consider, for example, the case of 2-in.-dia. bar extruded through a seven-hole die from a 16-in.-dia. billet. Taking into consideration the total cross-sectional area of the bars, the extrusion ratio is approximately 1 : 9; this means that the bars have a structure roughly corresponding with that of a 5 $\frac{1}{4}$ -in.-dia. bar extruded through a single-hole die from the same size of billet. A bar with a much less coarse structure would be produced by extruding, using a similar extrusion ratio, a smaller billet through a single-hole die, since small billets possess a much finer structure than large ones. The excessive coarseness of stringers of intermetallic compounds sometimes causes difficulty in forging, depending on the type of operation. Apart from this, forgings

made from smaller-diameter bars which have an unduly coarse structure tend to give poorer transverse tensile properties.

Fig. 7 (Plate XXXV) shows stringers of coarse inter-metallic-compound particles in a 2-in.-dia. multi-hole bar, while Fig. 8 (Plate XXXV) shows the typical size of intermetallic-compound particles in a bar of similar diameter extruded by the single-hole method. Another undesirable feature of bar extruded by the multi-hole method is that its structure, viewed in cross-section, is asymmetrical, being coarsest toward the side of the bar which was aligned with the centre of the cast billet; whereas large grain, if it does appear, tends to do so more on the opposite side of the bar. Thus a crescent of large grains may be formed. Cylinder-type forgings made from this kind of bar have often shown a large-grain region on one side only.

2. CAST STOCK

The main advantage of direct forging a cast ingot is that, by this method, larger forgings can be made than would be practicable with extruded bar. However, since it is possible to obtain extruded bar in sizes up to about 13 in. dia., most of the drop-forger's needs are satisfied in this way. Forgings which need to be made from larger sizes of stock are, in any case, more suited to production under the hydraulic press than by impact-forging.

Another possible advantage of using cast ingot is that forgings can be produced which have less-marked directional properties than are possible with extruded bar. In the cast condition the high-strength alloys D.T.D.683 and L.65, for instance, have good strength but relatively low ductility after heat-treatment. By thorough tri-axial working before forging to the finished shape, it is possible to improve this ductility in all directions, with perhaps a slight increase in strength as well. Forging to the final shape is then so carried out as to avoid the formation of a highly directional structure. The mechanical properties thus attained will still be lower than those obtaining in the longitudinal direction in a forging with pronounced directionality and, in some instances, may be only slightly better than those found in the transverse direction in such a forging. This method is more suited to the production of hand-forgings than to the making of closed-die forgings, since in the latter process directionality inevitably appears with the formation of the flash. It is well known that ductility is low in a direction normal to and across the plane of the flash.

Table I shows how tensile properties, both longitudinal and transverse, of a 7-in.-dia. L.65 cast billet improve with progressive reduction in cross-sectional area in a straight drawing-down operation.

These results were obtained from an unforged billet and from a stepped forging of square cross-section drawn out in the direction of the billet axis, each result being the mean of several tests. The forging was cut into several lengths and the pieces were heat-

treated in bulk on a normal production load. A reduction of over 40% was necessary to achieve specification properties in a longitudinal direction, and much higher reductions were required to give

TABLE I.—*The Relationship between Forging Reduction and Tensile Properties for Heat-Treated L.65 Alloy.*

Size	Reduction in Area, %	Average Tensile Properties					
		Longitudinal			Transverse		
		0-1% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Elong., %	Yield Stress, tons/in. ²	U.T.S., tons/in. ²	Elong., %
Specification		26	30	8
7 in. dia.	0	26.7	28.6	2	27.0	30.0	4
5½ in. square	31	26.0	29.7	5	27.3	28.8	5
4½ in. square	44	26.6	30.8	8	27.5	29.4	6
4 in. square	58	27.2	31.2	11	28.2	30.4	6
3½ in. square	70	27.1	31.4	13	27.6	31.2	5
2½ in. square	80	27.2	31.6	13	28.1	31.0	5
2 in. square	89	27.8	32.0	13	27.1	32.0	9
1½ in. square	95	28.1	32.0	12	27.2	31.5	7

tensile properties comparable with those obtained in forgings made from extruded bar. The transverse-test results are less consistent, but increased reduction tends to improve the tensile strength and elongation, whilst having little effect on the proof stress.

A cast ingot, when forged under the hammer, is much more prone to cracking than is extruded bar, especially in the high-strength alloys, and may therefore need special treatment. Surface-cracking may occur if oxide inclusions, cold shuts, inverse segregation, &c., have not been removed by machining. Some difficulty has on occasion been experienced in the forging of cast L.44 alloys, owing to the presence of oxide inclusions near the surface, despite an appreciable reduction of the cast diameter by machining. In the case of the L.65 stepped forging referred to above (which was quite successful), it was thought advisable to give a lengthy homogenizing treatment at 490°–500° C. before forging.

3. STOCK PRESSED FROM CAST INGOT

This type of forging stock possesses the same potential advantages as cast ingot, namely that it can be supplied in large sizes and that it may be used for making forgings with less-marked directional properties than forgings made from extruded bar; it also has the additional advantage that the stock is already well wrought before forging under the hammer begins and is therefore much less likely to crack. It is possible to supply pressed forging stock in a large variety of shapes and sizes, and with the grain disposed in whichever direction is required, within reasonable limits.

4. ROLLED STOCK

Several years ago a considerable quantity of rolled bar was used for making drop-forgings in the authors' works, and it was found to be quite as satisfactory for

the purpose as extruded bar. Of course, the particular advantage of using rolled bar lies in the fact that it is not susceptible to large-grain formation in the same way as is extruded bar. Nowadays certain types of forging, such as small pressure cylinders, are often required by their designers to be free from large grain; consequently, for such application rolled bar is considered the most suitable stock. Unfortunately, in recent years, it has been difficult to obtain supplies of rolled bar.

Rolled bar gives freedom from those other undesirable features peculiar to extrusions which were discussed above, but it may contain instead certain defects associated with rolling, such as seams or laps. In addition, the surface finish of rolled bar is not as good as that of extrusions. It is not possible to attain the same high tensile strength in rolled bar as in extruded stock, and since the typical extruded structure of the latter is often preserved almost unchanged in the finished forging, cut-up tests on forgings made from rolled bar may be expected to give a slightly lower strength than their counterparts from forgings made from extruded material. Nevertheless, there is generally no difficulty in meeting the designer's cut-up test requirements, provided that adequate reduction has been given in rolling the bar from the cast ingot.

For purposes of comparison, small cylinder-type forgings were made from extruded bar and also from rolled bar, both to specification L.65, at a forging temperature of 420° C. After heat-treatment, longitudinal and transverse tests were carried out on each, and the results are shown in Table II.

TABLE II.—Comparison of Tensile Properties of Small Forgings Made from Extruded and from Rolled Bar.

Forging A made from 2-in.-dia. extruded bar.
Forging B made from 2-in.-dia. rolled bar.

Forging	Test Direction	0.1% Proof Stress, tons/in. ²	Approx. Yield Stress, tons/in. ²	U.T.S., tons/in. ²	Elong., %
A	Long.	27.7	...	31.4	12
	Trans.	...	28.5	30.0	7
	"	...	27.5	30.0	8
B	Long.	27.0	...	31.2	12
	Trans.	...	27.0	30.0	8
	"	...	27.0	29.5	8

There is little to choose between the two forgings, though proof and yield stresses are slightly higher in the forging made from extruded bar. However, the rolled bar used in this instance had been rolled only from a 4-in.-dia. ingot, and if the rolling reduction had been greater, the longitudinal strength would probably have been higher. Macro-sections revealed a shallow peripheral coarse-grain area in the forging made from extruded bar, whereas the other had a uniformly fine-grained structure.

Another possible application of rolled forging stock is in the making of large forgings with a thickness

small in relation to their area. These may conveniently be made from cast rolling slabs which have been rolled to a suitable thickness.

To sum up, the forger's choice of stock should be governed by the following considerations :

(1) Extruded bar, if free from the defects discussed, is the most suitable general-purpose stock, especially for small stampings, but difficulties are always liable to arise from large grain on back-end portions of extrusions unless bars produced by the lubricated extrusion method are used. This type of bar, however, needs to be turned before forging. Large grains are rarely encountered in the case of the alloy D.T.D.683, and extruded bar can usually be employed on all types of jobs.

(2) Rolled bar is considered to be preferable to extruded bar for making stampings which it is essential to produce free from coarse grain.

(3) Cast or, to a greater degree, pressed stock is useful for making forgings larger than can conveniently be made from extruded stock, and also for making forgings free from undue directionality.

V.—HEAT-TREATMENT

The general principles and practice of heat-treating aluminium alloys are well known, and it is proposed to confine discussion here to some special considerations relating to the heat-treatment of forgings.

1. PLANT FOR SOLUTION-TREATMENT

Solution-treatment is carried out at temperatures between 460° and 550° C., and the types of furnace available have been reviewed by Evans, Hancock, Haywood, and McMullen,³ by Waight,⁴ and by Paton.⁵ A batch-type electric pit furnace, with an electrically heated quench tank and a relatively high-speed hoist, is very suitable for the purpose. The quench tank should be situated as near as is practicable to the furnace, so that quenching can be as rapid as possible to develop optimum mechanical properties and corrosion-resistance in the forgings. Automatic potentiometric temperature controllers and recorders are essential and, as recommended by Evans *et al.*,³ a safety controller should also be installed to cut off the current before the load reaches the overheating temperature in the event of the controller failing. Quenching is frequently carried out in water at 70°–85° C. and in boiling water, and specially designed quench tanks are necessary to deal with the great volumes of steam emitted; in addition, the top of the quench tank must be sealed to prevent the ejection of boiling water. The danger of this occurring can be considerable when loads of 25–30 cwt. are being quenched. Present-day quench tanks are therefore fitted with ducts to carry off the steam, and the tank is sealed by fitting a cover on the hoist rope at a suitable height, so that when the load is immersed, the lid fits over the tank.

Table III gives the results of a test carried out on a furnace of the above type.

TABLE III.—*Details of Test on an Electrical Solution-Treatment Furnace.*

Load: 16 cwt. of D.T.D.130A Alloy

Time	K.W.H. Reading	K.V.A.H. Reading	K.V.A.R.H.	Temp. on Furnace Recorder, °C.	Thermocouple Temp., °C.		
					Top	Bottom	Forging
1.50 p.m.	Load in furnace						
1.50 "	771	779	3.9	490
2.25 "	890	900	4.4	530	478	429	246
4.04 "	1052	1053	5.9	525	523	519	505
4.35 "	1082	1096	6.4	525	527	523	521
7.0 "	1175	1187	8.5	525	528	526	526
7.01 "	Load out						
Total 5 hr., 10 min.	} 404	408					

For this purpose, three thermocouples were inserted, two in free air at the top and bottom of the furnace and one in a forging situated on the bottom shelf of the charger or cage. Measurements were made at 10-min. intervals for 5 hr., but for the present purpose only those readings which are of interest in showing the uniformity of conditions in the furnace and the rate of heating are given, together with the power consumption.

It is well known that blistering may occur, especially on aluminium alloys containing magnesium, as a result of reaction with water vapour at high temperatures, and it is also known that sulphur compounds, which are always present in small but significant quantities in town gas, exert a pronounced catalytic effect on the reaction. Experiments which have been carried out in a town-gas-fired furnace, in which the charge is heated directly by the products of combustion, have shown that deterioration may be much more severe than in a simple case of blistering. Deterioration of constituents occurs largely at grain boundaries, and in exceptionally severe cases networks of grain-boundary films and even cracks may be produced.

The severity of attack is markedly dependent on the temperature of treatment, and is most pronounced in alloys requiring solution-treatment at about 530° C., such as D.T.D.130A and D.T.D.731. A lesser effect is produced on the Duralumin-type alloys, solution-treated at about 500°–505° C., whilst D.T.D.683, despite a high magnesium content, is relatively little affected at its solution-treatment temperature of 460° C. Various methods have been described for minimizing the reaction with water vapour, such as introducing into the furnace, or applying to the metal surfaces, small quantities of creosote, tallow, other hydrocarbons, or sodium fluoborate. Anodic oxidation is a very effective, though somewhat expensive, method of protection, whilst chemical oxidation, by a method such as the M.B.V. process, has been found to be a relatively cheap and effective method of preventing excessive water-vapour penetration.

Some deterioration of forgings can also occur in

electric furnaces if water vapour is present, and Ransley⁶ has shown that the extent of gas absorption is very greatly increased by the presence of relatively small amounts of sulphur dioxide or hydrogen sulphide. He suggests that sulphur may be introduced into the furnace atmosphere by means of residual lubricant on the surface of the metal. This subject has become of great importance owing to the practice of heat-treating large forgings after rough machining, and where the amount of final machining is small the components are sometimes anodized.

2. PLANT FOR PRECIPITATION-TREATMENT

Precipitation-treatment is generally carried out between 120° and 220° C., and the various types of equipment available have been discussed by Evans *et al.*,³ by Waight,⁴ and by Paton.⁵ Whichever type is used, it should possess automatic temperature controllers and recorder. The most suitable type of equipment for aluminium alloy forgings is considered to be an electrically heated, forced-air-circulation type of pit furnace, used in conjunction with a similar high-temperature furnace, as previously described. This may be placed adjacent to the quenching tank and arranged so that the loaded charger can be fed into it immediately after quenching. For economical operation of heat-treatment plant on a continuous basis, more low-temperature furnaces may be required than solution-treatment furnaces, because as a general rule the duration of precipitation-treatment is greater than that of solution-treatment.

Gas-fired furnaces may be used for precipitation-treatments, even if they are of the type in which the charge is exposed to the products of combustion, for within the relevant temperature range, there is no danger of appreciable gas absorption. However, as pointed out by Paton,⁵ for automatic control, gas-fired furnaces need more pyrometric equipment.

Salt-baths for precipitation-treatment are comparatively cheap in initial installation costs, but are rather expensive to run, mainly as a result of salt drag-out losses, which are likely to be greater than in high-temperature salt-baths because of the lower fluidity of the salt. In order to reduce these losses, a load when removed from the bath should be allowed to drain for a few minutes before it is transferred to the wash tank. Even so, frequent replenishment is required. Residual salt clinging to forgings is not easily removed in the wash and is liable to set up corrosion; it is therefore essential that pickling—which is carried out in any case before inspection—should be done almost immediately.

A real disadvantage of salt-baths for precipitation is that they cannot be used below about 150° C. and are therefore useless for D.T.D.683 alloy, which is aged at about 135° C. This is an important consideration, since forgings in this alloy constitute a considerable proportion of the total made today. If salt-baths are used, they should be electrically heated by means of immersion-heaters.

3. GENERAL PROCEDURE FOR HEAT-TREATMENT

(a) *Solution-Treatment*

Typical compositions for heat-treatable forging alloys are shown in Table IV.

TABLE IV.—*Typical Compositions of Aluminium Forging Alloys.*

Specification No.	Cu, %	Mg, %	Si, %	Fe, %	Mn, %	Ni, %	Zn, %	Ti, %
D.T.D.683 .	0.5	2.6	0.2	0.3	0.5	...	5.6	0.07
L.65, L.64 .	4.3	0.7	0.8	0.5	0.7
D.T.D.731 .	2.4	1.5	0.2	1.0	...	1.2	...	0.07
D.T.D.130A .	2.2	0.9	0.9	0.9	...	1.1	...	0.07
D.T.D.423B .	1.5	1.0	1.0	0.4	0.7
HF10	1.0	0.8	0.3	0.7

Finished forgings have the flash removed either by clipping or by band-sawing and are then ready for heat-treatment, except in those cases where rough machining is considered essential before heat-treatment. The objects of preliminary machining are : (i) The improvement of mechanical properties in the fully heat-treated condition by reduction of the mass-effect; in practice this is significant only on large forgings; and (ii) equally important is the reduction in unbalanced internal stresses which will be present after final machining. These stresses, if excessive, may cause distortion of the machined forging and result in increased susceptibility to stress-corrosion. For example, if cylinder-type forgings are heat-treated solid and bored out afterwards, the exposed surfaces in the bore may contain residual tensile stresses which could lead to stress-corrosion in certain environments.

The manner in which the furnace charger is loaded should be carefully considered with a view to permitting free circulation of the furnace atmosphere and fully effective quenching with a minimum of distortion and induced quenching stress. If one dimension of a forging is very different from the others, or if there are sudden changes in thickness, severe distortion may occur on quenching. This can sometimes be reduced by controlling the way in which the forging enters the water. For instance, long thin forgings should be quenched vertically, and it is therefore preferable to suspend or stand them upright. The preferred method for loading ring forgings, whose thickness is small in comparison with their internal diameter, is to stack them horizontally on a special charger, one on top of the other but separated by spacers, and to clamp the pile firmly at the top to prevent the column from moving. This method is found to minimize any tendency to distortion by twisting.

Solution-treatment usually lasts several hours, depending on both the alloy being treated and the size of the forgings. Time of soaking is calculated from the time when the load is up to temperature. There should be two recording thermocouples in the furnace, one giving the temperature of the air stream and one the actual temperature of the load; when the two traces coincide, the load is up to temperature.

With regard to the size-factor, a general rule commonly quoted is that at least 1 hr. is required for each inch of thickness. However, in the case of a partly machined forging, which may, for example, have had its maximum thickness reduced from 8 to 2 in., it is the original thickness which should be taken into account, since the time of solution-treatment required depends on the degree of fineness of the structure in respect of coring, soluble-constituent particle size, &c., which are unchanged by machining. Typical solution-treatment times and temperatures for medium-sized forgings are as follows :

L.64, L.65 .	4 hr. at 505° C.
D.T.D.130A, D.T.D.410, R.R.56 .	4 „ 530° C.
D.T.D.423B .	4 „ 520° C.
D.T.D.683 .	8 „ 460° C.
R.R.58, D.T.D.731 .	20 „ 530° C.
HF10 .	4 „ 535° C.

(When forgings need to be re-heat-treated, these times may be reduced.)

At the end of the necessary soaking period, the load is removed from the furnace and quenched as rapidly as possible. A cold-water quench gives maximum

TABLE V.—*The Effect of Temperature of Quenching Water on the Tensile Properties of Test-Pieces in the Heat-Treated Condition.*

Alloy	Quenching Temp., °C.	0.1% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Elongation, %
D.T.D.683	Specification :	27	32	7
	20	29.3	33.4	16
	40	29.6	33.6	14
	60	29.9	33.6	14
	80	29.6	33.2	14
	100	28.2	32.4	13
L.65	Specification :	26	30	8
	20	28.2	32.2	15
	40	28.0	32.3	14
	60	27.8	32.2	13
	80	26.6	30.8	12
	100	20.4	26.0	13
L.64	Specification :	15	25	15
	20	15.4	29.0	27
	40	14.6	28.6	25
	60	14.8	28.7	26
	80	13.6	28.0	28
	100	12.6	26.0	19
D.T.D.423B	Specification :	20	25	10
	20	21.6	26.0	19
	40	21.4	26.0	19
	60	21.2	26.0	19
	80	19.7	25.2	19
	100	15.2	20.9	19
D.T.D.130A	Specification :	21	27	10
	20	23.4	29.2	14
	40	22.6	29.0	14
	60	23.7	30.5	12
	80	21.8	28.5	10
	100	19.4	26.2	12
D.T.D.731	Specification :	20	27	6
	20	25.1	30.0	12
	40	23.8	29.2	12
	60	24.0	29.9	12
	80	22.8	29.6	13
	100	23.6	29.0	13

strength and corrosion-resistance, but sets up residual stresses greater than those found in forgings quenched in hot water. Quenching in boiling water minimizes the internal stress, but generally gives an appreciably lower strength. With most alloys it is the general practice to compromise by quenching in hot water at about 70° C. Table V gives some results of the effect of quenching at different temperatures on the mechanical properties of various alloys in the fully heat-treated condition. It will be seen that, as a general rule there is little fall in proof stress and tensile strength with quenching temperatures up to 60° C. The specification minima were still attained after a boiling-water quench for D.T.D.731 and D.T.D.683 alloys, but not for the other alloys. The fall in strength of L.65 and D.T.D.423B alloys after a boiling-water quench is particularly marked, especially in regard to proof stress. Since these results were obtained on 1½-in.-square test-pieces, quenched singly, they do not necessarily correspond with results which would be obtained on forgings quenched in a bulk load, for which the cooling rate from any particular quenching temperature might vary within fairly wide limits, depending largely on the size of the forgings. In forgings several inches thick, the mass-effect may be appreciable, causing a lower strength to be obtained in the core than near the surface.

(b) *Setting Operations*

Certain types of forging are susceptible to distortion on quenching, and this must be rectified as quickly as possible. It is known from experience which types of forgings require setting, and quenching is so arranged as to allow those responsible for setting adequate time to complete the job during the shift. The first essential for setting is a rigid table with a strong, smooth, and perfectly flat top made from steel plate. The type and extent of distortion of many forgings may be assessed by placing nominally flat surfaces in contact with the table; while one part of the forging is held firmly, pressure is then applied or blows struck in the appropriate position to correct the distortion. With more irregular shapes, it may be necessary to construct a special jig to hold the forging and to indicate when the distortion has been eliminated. Correction may be effected by flexure methods, employing some type of press, or by impact, using a hammer of a suitable size. Whichever method is used, precautions must be taken to avoid damaging the surface of the forging. Numerous blows or squeezes may be required before the distortion is removed. Some types of forging distort so greatly on quenching that it is essential to re-strike them in dies immediately after quenching. Even so, there is usually sufficient spring in the forging to prevent complete correction, so that a final setting operation is still needed. This method has to be employed, for example, on a forging in the form of a thin plate about 1 ft. square, supported by a rib on one side only, and decreasing in thickness from about $\frac{5}{16}$ in. on this side to

about 0.030 in. along the other edges. This type of forging distorts very badly on quenching.

If setting is not carried out within a few hours of quenching, it sometimes becomes so difficult that there is no alternative but to repeat the solution-treatment. This applies particularly to D.T.D.683 alloy and, to a slightly smaller extent, to the Duralumin-type alloys. Alloys such as R.R.56 and R.R.58 age-harden with appreciably less rapidity and allow greater latitude in setting.

(c) *Precipitation-Treatment*

As a general rule, if forgings do not need setting, precipitation-treatment is begun immediately after quenching. It is obviously most convenient to do this if the high-temperature and low-temperature furnaces are side by side, for then the same chargers can be used for both. However, it is permissible in most alloys to delay precipitation-treatment for a few hours at least—as is often necessitated by setting operations—though treatment of alloys of the magnesium-silicide type must be carried out within about 2 hr. of quenching; otherwise there is a deterioration in tensile properties, notably the proof stress. The following are typical precipitation-treatment times and temperatures:

Alloy	Treatment
L.65, HF15, D.T.D.130A, D.T.D.423B, HF10	10 hr. at 175° C.
D.T.D.683	12 " 135° C.
D.T.D.731	20 " 200° C.

Alloys in the first group may be treated for shorter times at a higher temperature, e.g. 185° C., but it has been found that the tensile properties thus obtained are not quite so good. It is immaterial whether forgings are allowed to cool in air or are cooled rapidly from the precipitation-treatment temperature. If salt-baths are used, the residual salt deposit is more easily removed if the load, after being allowed to drain for a few minutes, is quenched in water.

An additional heat-treatment occasionally specified by designers is a stress-relief anneal after final machining. This is designed to remove any stresses induced as a result of the very rapid removal of metal in automatic machining, and lasts for about 1 hr. at the normal precipitation-treatment temperature. Since forgings that are given this treatment are already down to finished size and are often anodized also, careful handling is very important if mechanical damage is to be avoided.

VI.—PICKLING AND INSPECTION

1. PICKLING

After heat-treatment, forgings are covered with a coating of oxide which must be removed before they can be efficiently inspected. The use of sodium hydroxide solution, one of the most effective agents for cleaning aluminium alloys, is not permitted, because, it is said, nascent hydrogen penetrates the surface layers and tends to reduce the fatigue

strength. The alternative recommended solutions are: (a) 9–12% H_2SO_4 + 0.75–1.5% NaF, (b) 20% orthophosphoric acid + 0.5% HF, (c) 10% H_2SO_4 + 4% KF, and (d) 10% H_2SO_4 + 1% HF. Of these the solutions containing H_2SO_4 are preferred. Forgings are immersed for several minutes in solution at about 20° C. The activity of the solution may be maintained by regular additions of fluoride and, less frequently, acid, until these are no longer effective; the solution must then be discarded. It is usual to follow the sulphuric-fluoride treatment by immersion for about 1 min. in 50% nitric acid to remove the black deposit produced on forgings in copper-containing alloys. Most of the acid is removed from the forgings by a cold-water rinse, and forgings are finally washed in warm water, so that they dry almost immediately on unloading.

It is permissible to use a caustic-soda etch on partly made forgings before intermediate grinding operations, and this is very effective in revealing surface defects. The solution used contains about 3% NaOH in water, and is maintained at 60°–70° C. Whichever pickling solution is used, care must be taken to avoid etching for too long, since this produces a roughened surface which tends to conceal defects and also to spoil the appearance of finished forgings. Furthermore, prolonged immersion in caustic soda solution may produce slight intercrystalline attack.

2. FINAL INSPECTION

The general inspection and testing requirements for aluminium alloy forgings to be used in aircraft are given in British Standard L.100.

Visual inspection of every forging is carried out, and any defects found are removed if practicable. Good lighting is essential, because some defects are exceedingly small; magnifying glasses are used when necessary. An experienced inspector knows which parts of a forging are most prone to show defects, and he gives particular attention to these places. Such danger spots include the flash area, radii between web and ribs, and any sharp bends where folds are likely to occur. If defects do not extend far below the surface, they are removed by filing in a direction at right angles to that of the crack, so that it is immediately apparent when the defect has been eliminated. With deeper cracks, flexible-shaft rotary cutters are used. If necessary, an estimate of the depth is first formed by filing across the crack with a triangular-shaped file until the bottom is reached. The rotary cutter is then used to remove metal to this depth. As a check on the complete removal of the defect, the surface may be finally smooth-filed. Defects are sometimes situated in such positions that it is impossible to use a file effectively, and rotary cutters alone have then to be used. The final cut should be a fine one to avoid the possibility of concealing a crack still present.

If, after removal of a defect, the forging is under-

size at that point, it is put aside for re-striking in the dies. Provided that the defect was not too deep and the general thickness of the forging is sufficient, the forging may be reclaimed in this way. For re-striking or "tapping", the forging is reheated, and hence it must subsequently be heat-treated again. It is important, when removing defects, not to leave sharp grooves or depressions, because these are likely to close up and form folds. The sides of the depression are therefore smoothed out so as to blend gradually into the general contour. A further point to bear in mind is that excessive local removal of metal may cause the grain flow to be materially altered in that position when the forging is re-struck. Local distortion of the fibre may have an adverse effect on the properties of a forging, especially if it occurs in an area of thin section.

Crack detection is facilitated by the anodic oxidation of forgings, using the chromic acid process, and it is general practice to carry this out on all finished aircraft forgings. They may also be anodized at an intermediate stage in their making, so as to ensure that all serious defects are removed before the pieces are forged to finished size. Before anodizing, forgings are "dressed", that is to say, the flash lines are filed and any surface roughness is removed; defects obvious at this stage are also eliminated. Chromic acid anodizing provides a very searching test for cracks, since the electrolyte penetrates them and subsequently seeps out, leaving a permanent brown stain in the surface oxide film. After anodizing, forgings are rinsed only for as long as is necessary to wash off surplus chromic acid without removing that which has penetrated the cracks. However, if the rinse is too short, some chromic acid may remain on the surface and give misleading stains. The anodizing process has an advantage over etching methods of crack detection in that it may be used on fully machined forgings without any reduction in dimensions, at the same time giving them a corrosion-resistant coating.

Generally speaking, internal cracks in forgings can be detected only by ultrasonic testing. Occasionally they become apparent when the core of a forging is partly removed by machining or when the crack comes to the surface through the flash. Ultrasonic testing, however, has decided limitations when applied to forgings, and it has not become established as a standard method of testing in the industry. The method may be successfully used on forgings of relatively simple shape, but it is of no great use for the majority of forgings, because of the difficulty of scanning thoroughly and obtaining reliable echoes unaffected by irregular shape and thickness. It may be possible to condemn certain forgings as having definite internal defects, but it is not easy to test forgings so thoroughly that freedom from such defects can be assured. Most internal defects in forgings result from the use of unsound stock, and it is comparatively rare for defects to be produced by bad forging practice. Thus the greatest freedom from such defects may be assured by adequate testing of the

stock itself before forging. The ultrasonic testing of the cast ingot is of particular importance, because it is at the casting stage that most of those defects may arise which will ultimately appear as internal defects in forgings.

3. TYPES OF DEFECT

It is important to be able to recognize the different types of defect and to assess the probable reasons for their occurrence, so that they may be avoided in future production. The main types of defect encountered in aluminium alloy forgings, together with their causes, are dealt with below.

(a) *Folds or Chops*

Folds are generally due to incorrect shaping of the dummy or incorrect placing of the dummy in the die. Some forging shapes are so difficult to produce without introducing folds that it is necessary to employ two sets of dies. The first set is designed to convert the dummy to a shape roughly resembling that of the final forging; the rough forging is then transferred to finishing dies. Folds are often formed where radii are inadequate, even if the correct forging technique is used. Occasionally a series of folds is formed around that part of the surface originating from the circumference of the extruded bar, as a result of recrystallization to give large grains during preheating and subsequent wrinkling. Folds may usually be recognized in macro-sections by the way in which the fibre is distorted around them; in micro-sections, they are invariably seen to contain entrapped oxide.

(b) *Surface Cracks*

These may be due to: (i) inefficient shaping of the dummy, so that excessive surface tensile stresses are set up in subsequent die-forging; (ii) the use of bar which has been overheated in extrusion; (iii) defects such as laps or oxide inclusions in cast stock; (iv) forging at too high temperature or with a rapid succession of very heavy blows, so that overheating occurs; (v) surface ruptures in large-grain areas, owing to the lower strength of large-grain structure; (vi) overheating in heat-treatment; and (vii) gas absorption due to preheating at unduly high temperatures.

(c) *Flash-line Cracks*

These may be due to the following causes or combinations of them:

(i) *Forging Above the Normal Temperature Range* (but below the solidus), so that local overheating may occur owing to a slight rise in temperature. When the die has been filled, surplus metal is forced out at the flash. In general, because of friction between the forging and the die, the flow of metal takes place at some depth from the die surface, and considerable heat may be generated in the intervening area between the moving metal and a relatively stationary zone close to the die. This is analogous to the conditions set up during the extrusion of aluminium alloys

described by Smith,⁷ and, in a similar way, overheating may occur in the region of maximum shear stress, leading to cracks which appear in the flash-line.

The same effect may be produced even with a normal forging temperature, if a rapid succession of heavy blows is given in an attempt to effect a large reduction in thickness. Local overheating may sometimes be found microscopically associated with flash-line cracks, but its detection is made more difficult if the forging has been subsequently heat-treated. It usually extends no more than a few thousandths of an inch from the crack.

(ii) *Unsuitable Die Design*.—If the design is such as to increase irregularity of metal flow in the region of the flash, there is an increased tendency to flash-line cracking. An example of this has already been discussed—the case of a forging with thin vertical ribs adjacent to the flash. The provision of inadequate radii at the base of the ribs means that the metal contained in the ribs is by-passed by metal flowing out from the web, and the shear stresses are so great in the very restricted zone between the relatively stationary metal and the moving metal that shear cracking may easily occur. If substantial radii are provided, the intermediate zone between the rapidly moving and the relatively stationary metal is much wider, and the stresses set up may be more easily accommodated without fracture.

It is to be noted that flash-line cracks due to the foregoing reasons are usually straight and occur not in the centre of the flash zone, but along or near the edge of it; in some cases double cracks are produced with a spacing between them which is roughly equal to the thickness of the flash.

(iii) *Overheating During Solution-Treatment*.—If the solidus is exceeded in heat-treatment, an intergranular network of liquid is liable to be produced, and the severe stresses imposed by quenching may cause intergranular cracking.

These cracks usually follow the grain direction and are therefore more likely to come to the surface in the flash than elsewhere in the forging, though a macro-section taken normal to the flash often reveals a number of other internal cracks remote from the flash. If a forging containing flash-line cracks due to this cause is examined microscopically, evidence of overheating in the form either of boundary liquid or eutectic "rosettes" is found throughout the forging, instead of only in the immediate vicinity of cracks, as is usually the case when these are produced in forging. Furthermore, there will be no indication of partial re-solution of the eutectic which may have occurred during heat-treatment if the liquation has actually taken place during forging.

(iv) *The Use of Internally Unsound Stock*.—It is possible that if bar or ingot is used which contains internal defects such as cracks, laminations, or oxide films, these flaws, although originally at some depth from the surface, may be forced into the flash and show up as cracks after the forging has been trimmed.

(d) *Internal Cracks*

Internal cracks can usually be traced to unsoundness in the forging stock, as has already been stated. It is comparatively rare for internal cracks to occur during forging without some surface cracks or end-bursting appearing at the same time.

Minute internal cracks are sometimes produced, during forging, around excessively coarse particles or stringers of intermetallic compound which interfere with regular metal flow and cause local fracture. These are revealed only if brought to the surface by machining. Machined forgings may be rejected because of the presence of such inclusions, even though cracks have not been produced.

(e) *Blisters*

Blisters usually become apparent after heat-treatment, being due to gas absorption during the treatment. Their formation is facilitated by the existence of sub-surface discontinuities such as a double skin. Occasionally areas of double skin are formed locally during forging by the shearing of a very thin surface layer of metal. This type of defect is confined mainly to surfaces more or less vertical in the die, and if blisters are fairly large and appear at random over the surface of the forging, it is generally found that the double skin was already present in the extruded bar stock. If the double skin revealed by the blisters is very shallow, as is often the case, it may be possible to grind it off; if not, the forgings may have to be scrapped. As previously stated, electric furnaces give greatest freedom from gas absorption and blistering, whilst anodic or chemical oxidation, or the addition of an inhibiting agent such as creosote to the furnace atmosphere, helps to minimize them.

(f) *Poor Surface Quality*

This is usually due to faulty die preparation or to deterioration of the die surface. The die surfaces should be well polished, but they deteriorate in use and must be re-polished whenever roughness becomes apparent; otherwise much extra work is entailed in grinding the forgings smooth. Eventually it becomes necessary to re-sink the impression in order to maintain the correct dimensions. When dies are not in use, the impressions are covered with a layer of grease to prevent corrosion.

Sometimes surface roughness is caused by over-pickling the forgings, and the appearance in such cases is easily recognized.

(g) *Dimensional Defects*

Since a lead proof or sample forging is always made from new dies and approved by the customer before full-scale production is begun, it is assumed when inspecting forgings that the dies are dimensionally correct. Nevertheless it is still possible to produce forgings of incorrect dimensions from such dies, for they may have been misaligned before stamping, or they may have moved laterally relative to each other

during the operation. The resultant forging is said to be off-set and is liable to be damaged round the edges if the flash is removed by clipping. A forging may be too thick, owing to an excessive thickness of flash, and in other cases it may be found that bosses are under size as a result of incomplete filling of the die. In all these cases it is usually possible to correct the forgings by re-striking. This cannot, of course, be done if too thin a flash has been left, so that the forging as a whole is under size.

(h) *Large Grain*

In aluminium forging alloys large grain is almost invariably due to the use of unsatisfactory extruded bar, and it therefore appears in the surface layers of forgings. Its presence is not always revealed by the normal etching procedure, since it may be covered by a "vener" of fine grains. In such cases it shows up only if part of the surface layers is removed before etching. When the layer of coarse grain is only superficial, it may be machined or ground off, but when it is severe, it often necessitates the rejection of the forgings.

A tendency to recrystallize to give large grains is very rarely induced by the forging process alone, if normal forging temperatures are adhered to and a critical amount of strain is not left in the metal.

(i) *Incorrect Grain Flow*

Before the bulk production of forgings is begun, a forging is made in the manner which, it has been decided, will give the most satisfactory grain flow, and this is checked by taking an appropriate section or sections. When the trial forging has been approved, all subsequent stampings out of the dies should be made in the same way, so as to avoid wrong grain flow.

(j) *Soft Spots*

Soft spots, which are due to uneven quenching, often show up as comparatively dull patches after pickling, and are better seen after filing. They are most frequently found on forgings quenched in boiling water, and it is the practice to check such forgings carefully for any sign of soft spots and to measure the hardness at several different points. The spots may be minimized by correct spacing of the load on the heat-treatment charger.

VII.—MECHANICAL PROPERTIES AND METALLURGICAL STRUCTURE OF FORGINGS

1. MECHANICAL TESTING

(a) *Tensile Tests*

Each batch of forgings heat-treated is represented by at least one set of three control test-bars made from the same material as the forgings. Test-bars are usually forged to about $1\frac{1}{2}$ in. square at the same time as the forgings they represent are made, but if the bar stock is small, control samples are heat-treated without forging. These control samples merely

establish the characteristic response to heat-treatment of the material in question, and test figures obtained from them do not represent the mechanical properties of actual forgings. These are checked by cutting test-pieces from various locations in heat-treated forgings and testing them according to the AX and BX procedures laid down in British Standard L.100.

The locations of tests are specified by the designers of the forging, and acceptable mechanical properties are agreed between the designers and manufacturers. These cut-up tests are carried out on one forging from the first batch made from new dies and on further forgings taken at intervals according to the requirements of L.100.

In certain cases, at the request of the designer, L.100 Testing Procedure C is adopted, a test-piece being forged integrally with each forging. Wherever possible, when cut-up tests are done, a standard-sized test-piece is taken and an actual proof stress is determined; in other cases Tensometer test-pieces are taken and the yield point, which approximates to the 0.2% proof stress, is determined from the load/extension diagram. Typical requirements for longitudinal and transverse cut-up tests in forgings of various alloys are given in Table VI.

TABLE VI.—*Typical Requirements for Tensile Tests from Forgings.*

Alloy	Direction of Test-Piece	0.1% Proof Stress, tons/in. ²	Yield Stress, tons/in. ²	U.T.S., tons/in. ²	Elongation, %
D.T.D.683	Long.	25.5	27	31	7
	Trans.	23.5	25	29	4
L.65	Long.	23.5	25	29	8
	Trans.	21.5	23	26	4
D.T.D.423	Long.	18	19	24	8
	Trans.	16	17	22	6

The tensile properties of aluminium alloy forgings vary considerably according to the angle between the axis of the test-piece and the grain or fibre of the forging. An experiment was carried out with the object of showing this relationship for several angles intermediate between longitudinal and transverse tests. A suitable length of 5-in. square bar was

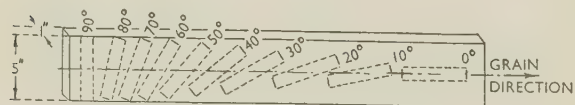


FIG. 12.—Positions of Tensile Test-Pieces Taken from Forged Bars at Various Angles to the Grain Direction.

drawn down in each of the alloys D.T.D.683 and L.65, in the former case from 8-in.-dia. extruded bar and in the latter case from a 7-in.-dia. extrusion. From the centre of each of these, two longitudinal slices, 5 in. wide \times 1 in. thick, were cut and given a normal heat-treatment. Afterwards, test-pieces were

cut from each slice as shown in Fig. 12, so that duplicate sets were obtained in each alloy.

The mean results of the tests are shown in Fig. 13. There is a general similarity between the graphs for

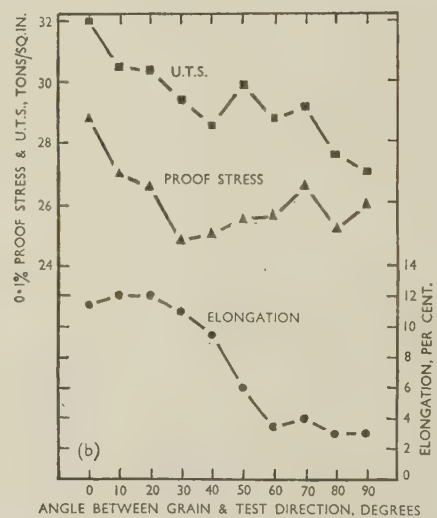
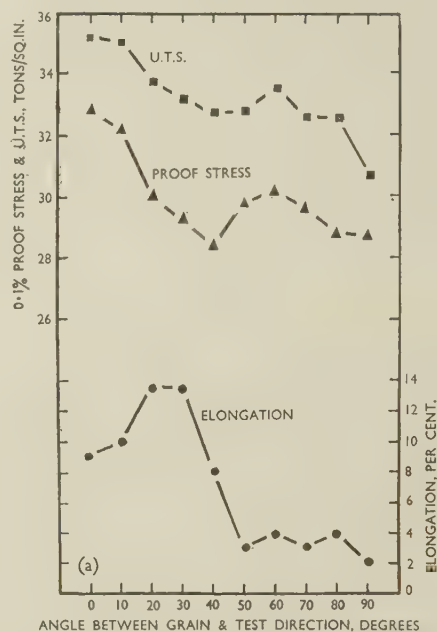


FIG. 13.—The Effect of Varying the Angle Between Grain Direction and Axis of Test-Piece on Tensile Properties. (a) In forged D.T.D.683 alloy, and (b) in forged L.65 alloy.

the two alloys; an appreciable reduction in strength occurs even at 10° to the grain, and both the proof stress and the tensile strength continue to decline with increase in the angle up to 30° or 40° and then improve to some extent. Finally, there is a further fall in strength with increase to 90° in the angle between the test-piece and the grain direction. Minimum proof-stress values were given by tests at 40° to the grain for D.T.D.683 alloy and at 30° to the grain for L.65; both alloys give minimum U.T.S. values at 90° to the grain.

Maximum elongation values were found in tests at 20°–30° to the grain for D.T.D.683 alloy and at 10°–20° for L.65. At angles of 40°–50° to the grain, elongation was reduced, and at angles of 60°–90°, elongation averaged 3–4% for both alloys. These results indicate that, from the point of view of ductility, any test on these two alloys taken at an angle of more than 40° to the grain direction must be regarded as a transverse test. Examination of the fractures showed that, whereas their appearance was little affected by the grain direction up to angles of 30°, in tests at 40° or more to the grain, they tend to occur roughly parallel with the fibre.

A similar pattern of behaviour to that shown in these tests has been observed in a comparable series of tests on D.T.D.683 extruded bar.

The mechanical properties of aluminium alloy forgings depend, apart from solution- and precipitation-hardening effects, on several structural features, namely grain structure, coring or banding, and the amount and disposition of intermetallic-compound particles. It is generally recommended that forgings made from extruded bar should be forged at as high a temperature as possible, consistent with the avoidance of overheating, so as to prevent recrystallization and preserve as far as possible the potentially high mechanical properties of the extruded bar, which are due to the "extrusion effect". In practice, it is difficult to prevent recrystallization, and the longitudinal tensile strength of forgings is usually lower than that of the bar from which they have been made, especially if the recrystallized grain-size is large.

As pointed out by Smith,⁷ those elements which are added to the high-strength alloys to raise their recrystallization temperature—manganese and chromium, in particular—may also have undesirable effects, such as hindering diffusion and lowering the transverse ductility, as well as reducing the forgeability. Transverse mechanical properties are more sensitive than longitudinal ones to the effect of banding and intermetallic-compound distribution, which may be observed only in micro-sections, as distinct from the actual grain structure, which is apparent in a macro-section. The more pronounced and directional this banding is, and the coarser the intermetallic-compound stringers, the poorer will be the transverse ductility. Fig. 9 (Plate XXXV) shows part of a typical fracture in a transverse test-piece taken from a D.T.D.683 forging made from 8-in.-dia. extruded bar. The structure is banded, and fracture has occurred in steps roughly parallel with the fibre.

A distinction needs to be made here between short and long transverse tests. The longitudinal test is taken to be one carried out parallel to the direction of working in which the greatest dimensional increase has occurred; the short transverse test may be defined as a test carried out parallel to the direction in which the reduction in thickness from the cast ingot is greatest, or a test which cuts the greatest possible amount of fibres. The longitudinal test normally gives the best possible combination of strength and

ductility, whereas the short transverse test-piece, though it may have good strength, is nearly always lacking in ductility. Tensile tests taken across the third dimension of a forging, i.e. perpendicular to both the longitudinal and short transverse directions, may give properties varying over the full range between these two tests, according to the manner in which working has been carried out. Normally tensile properties in this direction—the long transverse direction—are intermediate between those given by longitudinal and short transverse tests. This is illustrated by the following experiment.

Longitudinal and transverse (radial) tests were carried out on lengths of heat-treated 6-in. extruded bar of the alloys D.T.D.683 and L.65. Two lengths from the same bars were forged by laying on edge and flattening, so as to give plates 12 in. wide \times 1 $\frac{3}{8}$ in. thick. After heat-treatment, tensile test-pieces were taken from these forgings in the positions shown in Fig. 14. Tests E1–6 are from the extruded bar.

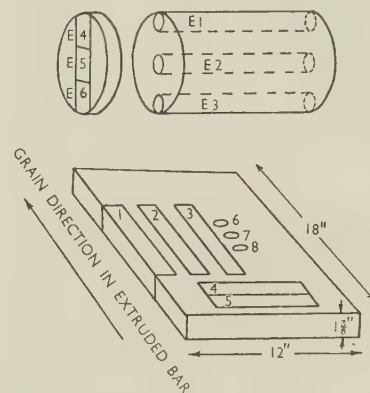


FIG. 14.—Tensile Test-Pieces Taken from Bar as Extruded and After Flattening.

Tests 1–8 are from the forging, 1–3 being longitudinal, 4 and 5 long transverse, and 6–8 short transverse. In longitudinal and long transverse tests, full-size test-pieces were taken, and actual proof stresses were measured; for short transverse tests, Tensometer test-pieces were used and approximate yield points were determined. The results are given in Table VII.

The high longitudinal strength in the as-extruded condition is reduced by forging, especially in the case of D.T.D.683 alloy. The long transverse tests from the forgings give strength values equal, or almost equal, to those of the longitudinal tests, with an only slightly lower elongation; the results of the short transverse tests from the forgings were equal to, or better than, those of the radial tests from the extrusions. The results given by Tensometer tests on L.65 alloy were somewhat erratic, this being an indication of the lack of reproducibility of results obtained from small test-pieces in transverse tests on certain materials.

Transverse ductility is generally poorer on large

forgings than on small ones, because of the greater coarseness of undissolved intermetallic compound particles. Coarse aggregates of these particles, if

TABLE VII.—Results of Tensile Tests on 6-in.-Dia. D.T.D.683 and L.65 Alloy Extruded Stock Before and After Flattening.

Position (see Fig. 14)	Type of Test *	D.T.D.683			L.65		
		0-1% Proof Stress (or Yield), tons/in. ²	U.T.S., tons/in. ²	Elong., %	0-1% Proof Stress (or Yield), tons/in. ²	U.T.S., tons/in. ²	Elong., %
E1	L	36.3	39.2	8.5	30.4	33.4	12
E2	L	36.0	39.2	10	27.6	31.5	12
E3	L	36.2	38.0	8	30.2	31.5	12
E4	T	30.5	31.5	3	... †	22.5	0
E5	T	30.0	31.5	3	26.5	28.0	3
E6	T	29.0	30.0	3	21.0	22.0	2
1	L	30.7	35.6	12	27.9	32.0	12
2	L	30.2	34.6	11	27.2	31.1	13
3	L	30.2	34.8	11	28.2	31.0	13
4	LT	30.7	35.2	9	26.6	30.9	10
5	LT	31.2	35.5	9	27.8	31.4	9
6	T	30.0	31.5	3	27.0	29.0	5
7	T	31.0	32.5	5	24.0	25.0	2
8	T	30.5	32.5	5	25.5	27.0	3

* L = longitudinal, LT = long transverse, and T = short transverse.
† Not measured.

present, are likely to have a greater effect on test-pieces of small cross-section, which accounts for the lack of reproducibility referred to.

(b) Hardness Tests

The standard hardness test for forgings is the Brinell, using a 10-mm. ball and 1000 kg. load, but the diamond pyramid hardness test may also be used. Each forging is tested, and sizeable forgings are tested in several places to guard against the possibility of soft spots. This is especially important on forgings quenched in boiling water.

Typical Brinell hardness ranges for different alloys are as follows:

	B.H.N.
D.T.D.683	154-185
L.65	138-165
L.64	107-117
D.T.D.423B	114-129
D.T.D.130A	121-148
D.T.D.731	117-129

Any forgings with a hardness lower than the minimum permissible value are returned to the furnace for re-heat-treatment.

2. MACRO-EXAMINATION

Macro-examination is carried out on a routine basis for checking the structure of forgings, the grain flow for which is specified by the designer. The plane in which the forging is sectioned is decided by the drawing indicating grain-flow requirements, and it is often necessary to etch more than one section to

show that the grain flow is exactly as specified. Macro-sections should not be taken in the plane of the flash, because the structure here is not representative of that in the rest of the forging, and true grain flow may be confused by the effect of lateral metal movement.

Macro-examination is used as a test of quality of forging stock, and in the case of extruded or rolled bar transverse slices are cut, and then solution-treated before being prepared and etched. By this means defects such as double skin, rolling laps, and tendency to form large grain may be detected. However, an etched slice of extruded bar showing no large grain is not very significant unless it is known to be taken from a position toward the back end of the extrusion.

The examination of macro-sections is also very useful in the investigation of defective forgings, and often helps to decide the causes of defects and their severity.

3. MICRO-EXAMINATION

Used in conjunction with macro-examination, micro-examination is an important part of the quality control of drop-forgings. Besides being used as an occasional check on the quality of forging stock, micro-sections are regularly taken from heat-treated forgings to confirm that there has been no overheating during heat-treatment. The main use of micro-examination is in the investigation of defects in forgings and forging stock, and it is usually possible thereby to determine whether these are due to faulty material, forging, heat-treatment, or any other cause. Thus the findings may suggest alterations in procedure to prevent recurrence of the defects, as illustrated by the following two examples. Fig. 10 (Plate XXXV) shows a series of folds containing entrapped oxide, in the radius between the rib and the web of a small forging. By enlarging this radius, defects such as these were subsequently avoided. In the second case, a length of 5-in.-dia. D.T.D.364 alloy bar cracked severely at the ends as soon as forging was attempted. Micro-examination of the bar revealed signs of severe overheating, (Fig. 11, Plate XXXV), which must have occurred during extrusion.

VIII.—MAGNESIUM ALLOY FORGING PRACTICE

The development of the ZW3 type of magnesium alloy has made possible the production of high-strength drop-forgings. The technique employed is in general the same as that for aluminium alloys. The forging temperature range is 300°-500° C., and the preheating equipment is the same as for aluminium alloys. Forced-air-circulation electric furnaces are to be preferred, but recirculated-atmosphere gas-fired furnaces have been used with success. As is well known, the preferred orientation which occurs on plastic deformation of magnesium gives rise to a directionality of properties.

During the free-forging operation the directional effect becomes apparent. Cast stock draws out or elongates easily and satisfactorily until the original cross-sectional area has been reduced by about 50%. Further working does not result in any elongation of the bar, but leads to bulging of the material from the sides. When the bar is then turned through 90° the effect is the same, and continued hammering in this manner leads to cracking of the bar along the corners.

TABLE VIII.—*Tensile Properties of Drop-Forging in D.T.D.729 Alloy (ZW3).*

Composition: Zinc 3, zirconium 0.7%, magnesium the remainder.

Size of Ring			Longitudinal Properties			Transverse Properties		
Dia., in.	Depth, in.	Thickness, in.	0.1% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Elong., % on 4√A	0.1% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Elong., % on 4√A
10.5	2.25	0.75	13.4 12.2	18.2 17.9	8 6	14.3 13.3	18.7 17.6	16 16
10.75	3.0	1	13.9 14.6	18.4 19.0	7 5	12.8 12.8	18.2 17.9	13 17
Specification D.T.D.729			11.0	17.0	8			

Tests taken on Tensometer test-pieces.
Transverse tests were across the depth of the ring.

Extruded bar cannot be worked by free forging. High directional characteristics have been imposed upon the material during the extrusion process, and any attempt to forge the material results in shear cracking. This means that extruded bar cannot be used for forgings which require dummieing or preforming. In the case of certain simply designed forgings, extruded bar can be drop-forged in dies when sawn lengths of the bar are placed directly in the impression. Even in these simple cases, extruded bar produced by

heavy reductions of cast stock cannot be drop-forged, and it is necessary to limit the use of extruded bar to that obtained by extruding cast billets of 4 or 5 in. in dia. Cast stock is therefore generally made the starting point of forgings and drop-forgings in ZW3 alloy.

The directional effect must be taken into account when deciding the form of the dummy to be laid in the die. A suitable size of cast stock must be chosen so that the reduction during preparatory forging does not exceed 40–50%. Material having this amount of reduction readily forges without cracking when supported by the die walls during the drop-forging operation.

Two mandrel-forged rings are shown in Fig. 5 (Plate XXXV), and their tensile properties are given in Table VIII.

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REFERENCES

1. F. E. Stokeld, *J. Inst. Metals*, 1949–50, **76**, 453.
2. R. G. Wilkinson and F. A. Fox, *ibid.*, 473.
3. C. J. Evans, P. F. Hancock, F. W. Haywood, and J. McMullen, *ibid.*, 1951–52, **80**, 255.
4. J. F. Waight, *ibid.*, 269.
5. C. P. Paton, *ibid.*, 311.
6. C. E. Ransley, *ibid.*, 1953–54, **82**, (12), 588 (discussion).
7. C. Smith, *ibid.*, 1949–50, **76**, 429.

1594 THE HEAT-TREATMENT, INSPECTION, AND TESTING OF WROUGHT NICKEL AND NICKEL ALLOYS *

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SYNOPSIS

The production of wrought nickel and nickel alloys is described, with particular reference to the heat-treatment, inspection, and testing procedures applied after all hot- or cold-working operations are completed; brief descriptions of the various working methods are also included. The materials dealt with are notable for their wide variety of special properties, and the testing and inspection methods adopted are necessarily referred to only in outline.

I.—INTRODUCTION

THE wide range of nickel-base alloys, and the number of forms in which such alloys are supplied, make it difficult to give any concise survey of the methods of control adopted in the final stages of production. Nickel and nickel alloys have many "special" properties, and it is therefore necessary to describe inspection and testing procedures adopted for alloys with, for example, particular magnetic properties, controlled thermal-expansion characteristics, a high degree of resistance to scaling, or outstanding resistance to creep. In addition to special tests of this character, the normal tests for mechanical properties and dimensional accuracy are carried out.

The alloys covered by this survey fall into three main groups:

(1) Nickel and its alloys with iron, cobalt, copper, manganese, and silicon. These are relatively soft and can be easily hot and cold worked.

(2) Nickel-chromium and nickel-chromium-iron alloys. These are notable for their high electrical resistance and their resistance to scaling at high temperatures. They are much more difficult to hot or cold work than the alloys of group (1).

(3) Creep-resisting alloys based on the nickel-chromium or nickel-chromium-cobalt systems. They are difficult to hot work and can be cold worked only by frequent inter-stage annealing.

These alloys are processed to most of the standard forms, which may be classified as follows:

(i) Rolled or extruded bar, often subsequently machined.

(ii) Forgings—square or rectangular bar, discs, rings or die-forgings.

(iii) Sheet and strip, down to 0.0007 in. thick.

(iv) Wire down to 0.0005 in. dia.

(v) Tube.

In the present paper attention is confined to the operations of heat-treatment, inspection, and testing which follow the forming processes, except that some aspects of the cold drawing of wire and tube are also described.

Since the procedure of handling and inspection is frequently the same for different alloys and for different forms of final products, it has been found convenient to describe the processes in general and to refer, at appropriate points, to the particular behaviour of special alloys or forms.

II.—COMPOSITION

Full chemical or spectrochemical analysis is made on all heats before the processing of ingots is begun. In addition tests designed to confirm the identity of an alloy are made from time to time, particularly in connection with forms of material, such as fine wire, which cannot be marked on the surface, but must carry labels.

For this purpose, qualitative observations of magnetic response are helpful and are often sufficient to distinguish between materials. Nickel itself is, of course, strongly magnetic below the Curie point (353° C.), and the nickel-iron alloys, except in a narrow range of composition around 30% nickel, are magnetic at normal temperature. The binary alloys with copper contents up to just above 30% are also magnetic at room temperature, and Monel (approximately 30% copper) is feebly magnetic. The precipitation-hardenable alloy K Monel, however, is non-magnetic at normal temperatures. The Curie point of nickel-chromium alloys falls to room temperature at about 7% chromium, and all commercial alloys based on the nickel-chromium system are normally non-magnetic. However, oxidation of such alloys

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results in a reduction of the chromium content of the surface layers, and it is quite common for such oxidized surfaces to show a magnetic response. Some nickel-iron-chromium alloys with chromium as high as 15% fall in the range of magnetic alloys at normal temperature, and the published data¹ are helpful in identifying alloys within this system.

By the use of chemical and electrochemical methods on a qualitative basis, it is possible to supplement magnetic observations and to identify all the nickel alloys in current production.

A quick test for distinguishing cobalt-containing alloys from cobalt-free alloys is to add a few spots of *aqua regia* to a ground or oxide-free surface. The presence of cobalt results in a typical blue coloration.

Nickel-chromium alloys containing titanium can be identified by treating the sample with sulphuric acid and diluting the solution with water; the addition of hydrogen peroxide then produces the distinctive yellow of per-titanic acid.

Iron-containing alloys are identified, and the iron content can be roughly assessed, by an electrolytic method, using a solution containing 2½% potassium thiocyanate and 1% sulphuric acid. The test consists essentially of passing an electric current through a filter paper moistened with the solution and placed on a clean surface of the material. A nickel wire forms the cathode and is touched on to the paper above the sample, using a potential of about 12 V. A red coloration indicates the presence of iron, and the intensity of coloration can give an indication of the iron content, particularly when comparative tests on known alloys are made under identical conditions.

The presence of manganese can be detected, and a rough estimate of the content made, by a similar method. A piece of wire of the alloy to be tested is made the anode in an electrolyte consisting of 100 c.c. saturated potassium bromate solution, 50 c.c. conc. sulphuric acid, and 100 c.c. water. The cathode is a pure nickel wire, and a potential difference of 6 V. is used, at about ¼ amp. The presence of manganese is indicated by the formation of a pink solution due to potassium permanganate, and the intensity of the coloration permits an estimate to be made of the manganese content.

As referred to later, measurements of specific resistivity are also helpful in identifying materials.

III.—PRODUCTION OF DIFFERENT FORMS

The final quality of material is, in many cases, dependent to a large extent on the early operations, and for this reason brief comment is made in this section on the procedure followed in the production of the different forms of material, with particular reference to the way in which such procedures are controlled by subsequent inspection. A description of the plant used for hot working nickel-base materials has been given by Barclay, Russell, and Williamson.² American practice has been described in a number of papers.³⁻⁶

1. ROLLED OR EXTRUDED BAR

Bar is hot rolled to sizes from about 4 to 0.375 in. dia.; broadly speaking, the methods used are those normal in rolling steel. For the nickel-chromium creep-resisting alloys of group (3), however, the hot-working temperature range is narrow, and this fact, combined with the high resistance to deformation which is characteristic of these alloys, necessarily limits the amount of deformation permissible between reheatings.

Extrusion of nickel, Monel, and the softer alloys has been carried out for many years, and this method of processing the harder alloys referred to in the previous paragraph has been facilitated by the introduction of glass as a lubricant.⁷

2. FORGINGS

For many reasons, including uniformity of structure and high output, rolling or extrusion is to be preferred to forging for the production of bar, but the number of different sections required sometimes renders forging necessary. Particularly in dealing with the creep-resisting alloys of group (3), for which the hot-working temperature range is narrow, there is a tendency to continue forging below the minimum temperature and thus to introduce "cold work". This can vary from point to point in the section, and on subsequent heat-treatment can lead to an irregular and undesirably large grain-size. Similar effects can arise in die-forging, for example of turbine blades, unless care is taken to ensure that the amount of deformation at the final stage is sufficient to avoid the critical amount of strain which leads to the growth of large grains. The suitable conditions of hot working and of die design have to be developed by essentially empirical methods, the forgings being sectioned and etched to reveal the grain-size; periodic checks of the same nature need to be made to ensure that changing conditions such as may arise from die wear have not led to undesirable structures.

3. SHEET AND STRIP

Machined ingots are initially hot worked either by breaking down on a Universal mill or by extrusion. The sheet bars are then hot rolled on a 3-high sheet mill, the finer gauges being finished by pack-rolling. Before cold rolling, the sheet is either bright-annealed in an atmosphere of partially burnt town gas (if the oxide is capable of being reduced by this gas), or batch-annealed in an air atmosphere, followed by shot-blasting or pickling (if, as for the chromium-containing alloys, the oxide is not readily reduced). Intermediate annealing of all materials is carried out in the "reducing" atmosphere.

4. WIRE

Wire in all the alloys is drawn from hot-rolled rod, 0.375 in. in dia., which, in coil form, is either bright-annealed or annealed and pickled. The lubricants used for drawing the softer materials are flour, hard

soap, and tallow. The harder nickel-chromium and nickel-chromium-iron alloys require lead coating in the initial and intermediate stages of drawing, and when the materials require annealing the lead must first be removed by pickling in 10% nitric acid; the wire is subsequently re-coated if necessary. In general, lead is used for nickel-chromium alloys down to 30 S.W.G., after which mineral oil is used to 43 S.W.G., and a water-soluble oil for the superfine sizes. Tungsten-carbide dies are used for drawing with all materials from the 0.375-in.-dia. rod to 0.032 in. dia. (21 S.W.G.), while for finer gauges diamond dies are employed. Continuous inspection and maintenance of dies are necessary to ensure that the wire produced is within the practical limits for each stage of drawing, and within the specification for gauge tolerance and ovality of the finished wire. Tungsten-carbide dies are withdrawn regularly for inspection and polishing, the period of service depending on the weight and quality of wire which has been drawn. Table I

TABLE I.—Average Weights of Wire Drawn Through Tungsten-Carbide Dies before Repolishing.

Wire Dia., in.	S.W.G.	Weight of Wire, lb.	
		80 : 20 Ni-Cr	Monel
0.036	20	255	...
0.040	19	500	...
0.064	16	2,080	...
0.104	12	4,000	...
0.128	10	10,000	30,000
0.144	9	16,540	35,500
0.245	100,000
0.290	200,000

TABLE II.—Target and Average Weights of Wire Drawn Through Diamond Dies before Repolishing.

Wire Dia., in.	S.W.G.	80 : 20 Ni-Cr			Monel		
		Target, lb.	Average before Polish		Target, lb.	Average before Polish	
			lb.	ft. × 10 ⁶		lb.	ft. × 10 ⁶
0.0007	0.5	0.365
0.0008	0.9	0.500
0.0016	48	...	5.9	0.820	...	6.9	0.95
0.0020	47	...	9.6	0.854
0.0024	46	...	12.3	0.752	...	15	0.92
0.0032	44	...	16.5	0.572	...	24	0.82
0.0040	42	10	24.6	0.546	20	50	1.10
0.0052	39	10	61	0.793	20	53	0.69
0.0068	37	25	69	0.674	50	128	0.97
0.0084	35	25	105	0.523	50	407	2.03
0.0100	33	50	146	0.514	100	604	2.12
0.0120	30½	50	196	0.478	100	580	1.42
0.0142	28½	175	502	0.703	200	840	1.47
0.0164	27	175	640	0.864	200	1380	1.81
0.0179	26	175	797	1.275
0.0200	25	200	1170	0.976	...	880	0.77
0.0220	24	200	1002	0.726
0.0236	23	250	880	0.538	...	1000	0.61
0.0275	22	250	940	0.422	...	1100	0.49
0.0320	21	250	726	0.250

indicates the weights of wire of different materials normally drawn through dies of different sizes before such withdrawal becomes necessary. In addition, periodic gauging of the drawn wire is carried out in

order to detect immediately any deterioration of the die. Repolishing to enlarge the die to the next gauge is normally carried out six or eight times before the die is scrapped. Diamond dies are treated similarly, being withdrawn for inspection and repolishing to the next larger gauge if necessary, after a certain target weight of material has been drawn. Table II gives the target weights of different materials for a variety of die sizes, together with average weights actually drawn before repolishing. Frequent inspection of the as-drawn wire is, of course, carried out and may lead to earlier withdrawal of a die. It is interesting to note from columns 5 and 8 of Table II that the average length of wire drawn before a die is repolished is practically independent of the gauge. Diamond dies may normally be repolished three or four times, although, for example, very fine wire dies starting at 48 S.W.G. can usually be enlarged as far as 36 S.W.G., and in exceptional cases as far as 33 S.W.G. before scrapping.

5. TUBE

In all nickel alloys, tube is produced by initial hot extrusion, followed by cold drawing. Billets for large-diameter tubes are hot pierced and extruded, using tallow and graphite, while for smaller-diameter tubes they are drilled and extruded, using glass as a lubricant. The extruded tubes are pickled and locally fettled, pointed by cold swaging, and cold drawn. Reductions per pass on outside diameter vary from $\frac{1}{16}$ to $\frac{3}{16}$ in., and in wall thickness from 10 to 25%. After each pass the tubes are degreased, annealed in a protective atmosphere, and re-pointed. After the first two draws, when any roughness from extrusion has been smoothed out, the tubes are pickled and fettled as required, and the same procedure is repeated before the final draw. Finished tube is straightened, cut to length, and heat-treated. Final inspection covers dimensional checks, pressure tests, and visual examination.

IV.—HEAT-TREATMENT

Final heat-treatment operations are of two types: (i) annealing, normally applied to sheet or wire products in order to soften them for subsequent working operations; and (ii) hardening, consisting of a solution-treatment followed by one or more precipitation-treatments, with the object of improving the mechanical properties. The bright annealing of nickel alloys has recently been described in some detail by Hartley and Bradbury.⁸

1. ANNEALING

(a) Sheet and Strip

The furnaces used for annealing sheet and strip are all electrically heated and are either batch-furnaces with an air atmosphere or continuous furnaces employing some form of controlled atmosphere. The annealing

temperature range suitable for nickel and its alloys is about 800°–1050° C., and the average time of treatment is about 15 min. Loads and heating-up times for batch furnaces, and belt loading and rate of flow in continuous furnaces, are adjusted to give the required conditions.

Three types of continuous furnace are in common use :

(i) *Belt furnaces*, in which stock is conveyed on a continuous woven-wire belt through the heating zone and adjacent water-jacketed cooling zone. Partially burnt town gas is used as protective atmosphere.

(ii) *Continuous strip-annealing furnaces*, in which strip below 0.030 in. in thickness is drawn through the heating and cooling zones by being wound on to a variable-speed rotating drum. Atmospheres in these furnaces may be either partially burnt town gas or cracked ammonia.

(iii) "*Pusher*" furnaces, in which the stock is carried through the furnace on 20-in.-square grids pushed forward mechanically at fixed intervals. The atmosphere used is partially burnt town gas.

In the case of all continuous-flow furnaces the length of the cooling zone is such that, with normal speeds of annealing, the material is well below the oxidation temperature before it is clear of the protective atmosphere.

(b) Wire

Two types of annealing treatment are given to wire, the first designed solely to soften the material and the second designed to produce in addition an electrically insulating oxide coating on wire to be used for closely wound resistors.

For simple annealing, continuous furnaces of two types are used :

(i) *Continuous-belt furnaces*, using an atmosphere of partially burnt town gas, which on nickel gives a bright-annealed surface and reduces the rate of oxidation of nickel-chromium alloys. Such furnaces are used where annealing is required in the early stages of wire drawing, the wire being loaded on to the belts in loose coils.

(ii) *Strand-annealing furnaces*. In this type of furnace a tube of Inconel (nominally nickel 78, chromium 15, and iron 7%) forms the electrically heated element. Inside this tube, and insulated electrically from it, are smaller Inconel tubes, up to ten in number, through each of which passes a strand of wire for annealing. An atmosphere of cracked ammonia is passed through and around the outside of these smaller work-tubes. The annealed wire finally passes through water-cooled tubes and is wound on to reels. Finished wire is subsequently spooled as a separate process.

Strand-annealing furnaces of the above type were found to be unsuitable for very fine wire, since the tension required to draw the wire through the furnace exceeded the breaking load of the wire at the annealing temperature. For example, 80 : 20 nickel-chromium wire of 0.002 in.-dia. breaks at a load of 0.4 oz. at 1000° C. A modified design has therefore been

adopted for use with wires below 40 S.W.G. A single tube is resistance-heated, the hot zone being only 28½ in. long and the cooling zone 16 in. long instead of about 12 and 6 ft., respectively, for the multi-strand furnace. Temperature control of the single-tube furnace is effected by the expansion of the furnace tube to operate a microswitch. The furnace temperature is 1050° C. for nickel-chromium wires, and at a speed of 5 ft./sec. for 46-gauge wire, the wire is in the heated zone for 0.5 sec. An atmosphere of cracked ammonia is used.

The insulating oxide film on nickel-copper wires is produced by treatment at 720° C. for 1 hr., in batch-furnaces. Wire coarser than 29 S.W.G. is treated in coil form, and in this case the oxygen content of the furnace atmosphere is reduced by burning two coal-gas flames within the furnace. This reduces the rate of oxidation and ensures an adherent oxide film. Wire finer than 29 S.W.G. is loosely spooled on metal reels made of Inconel, and in this case gas flames in the furnace are unnecessary.

The oxide film formed on nickel-chromium and nickel-iron-chromium wires by heating in air consists largely of chromium oxide and is too thin to give adequate insulation. To produce a satisfactory oxide layer, a thin electrodeposit of nickel is applied to the wire, which is then drawn to final size and oxidized.⁹ The exact conditions of oxidation depend on the gauge of the wire, but in all cases the treatment is carried out in an atmosphere of air at about 850° C.

2. PRECIPITATION-HARDENING TREATMENTS

For most precipitation-hardening treatments of alloys control of temperature is an important factor, since the resultant properties are critically dependent on the conditions of heating. This is particularly true for the nickel-base creep-resistant alloys of group (3). When bar of these alloys has subsequently to be forged, it is frequently supplied in the un-heat-treated condition, but bar for machining is usually fully heat-treated. Solution-treatment for alloys of this type is effected by heating at a temp. in the range 1050°–1200° C., for periods up to 8 hr. Horizontal, single-ended, batch-type electric furnaces are usually employed, for which the maximum load is about 400 lb. and the work takes about 2 hr. completely to reach temperature. The consequent uncertainty in the time of treatment is of no importance in treatments of 8 hours' duration.

Some of the shorter-period higher-temperature solution-treatments for these alloys are carried out in a gas-fired furnace which has a range of 750°–1250° C. A gas curtain, directed downwards across the full width of the chamber, prevents the entry of outside air and reduces scaling. Capacity is up to about 700 lb., and a maximum load of this size takes about 1½ hr. to attain temperature. In the case of a treatment involving times of only 1–2 hr. however, it is not possible to treat so large a charge, since variation due to slow heating would result in variable creep

properties. The charge is therefore limited to 400 lb., a mass which reaches temperature in about $\frac{1}{2}$ hr.

Owing to the need for correct nucleation of the precipitate in these alloys, their creep properties are dependent to some extent on the rate of cooling from the solution temperature. The optimum rate has been found to be approximately that given by normal air-cooling of bar of about $\frac{3}{4}$ –1 in. dia., and such treatment is satisfactory for most products. The only essential precaution is that the material should not be allowed to cool in a pile; there must be adequate access of air to all bars, since too slow a cooling rate results in intergranular precipitation, leading to brittle fractures under creep conditions. Water-quenching, on the other hand, is to be deprecated, since apart from its detrimental effect on the creep properties, severe longitudinal cracking may result, especially in the case of large sections.

Ageing treatments for this class of alloys are usually carried out at about 700° C.; electrically heated furnaces of the batch type used for solution-treatment are generally employed.

V.—INSPECTION METHODS

The inspection of finished or near-finished products for defects, can be divided into two categories: non-destructive examination for internal faults and surface inspection.

1. INSPECTION FOR INTERNAL DEFECTS

Three methods of non-destructive testing for internal defects have been used, viz. radiographic, ultrasonic, and eddy-current methods. Radiography by conventional methods, using 400-kV. plant, has been found of value in the examination of forgings of the creep-resistant nickel–chromium alloys. These alloys are susceptible to bursting if hot worked at temperatures unsuitable for the rate of deformation, and radiography has been used successfully to determine suitable conditions. Ultrasonic testing has, however, replaced radiography as a more routine procedure when the type of defect sought is known and the ultrasonic indication characteristic of its existence has been established. For the examination of relatively small components, such as turbine-blade forgings, a combined “transceiver” probe, with rubber diaphragm, has been found suitable.

Eddy-current examination has proved to be of great value in the examination of bar, particularly of the alloys of group (3), which have high electrical resistivity and are non-magnetic. The method is sensitive to both internal and surface defects, and is, therefore, most conveniently applied to machined bar on which surface defects have been reduced to a minimum. Extruded bar, and even hot-rolled bar, have also been successfully examined by this method. The equipment used is based on that developed by Förster,¹⁰ except that phase-sensitive detection is discarded in view of the high electrical resistivity of the alloys.

The apparatus is balanced with a sound bar, of the same diameter as the bars which are to be inspected, in position in the coils. Balance is considered to have been reached when the lowest possible reading on the voltmeter is obtained. Such factors as change of diameter, composition, hardness, and condition of heat-treatment can cause some loss of balance. Thus slight balancing adjustments may have to be made from bar to bar to allow for different cast analyses or variation in diameters, but these effects are small compared with the loss of balance resulting from defects in the bar.

The sensitivity of the apparatus to defects is greatest at the outside of the bar and falls off slightly towards the centre. For optimum sensitivity the internal diameter of the testing coils should be as close as possible to the diameter of the bar stock under test, and should be chosen so that the bar can pass through freely with a radial clearance of $\frac{1}{32}$ – $\frac{1}{8}$ in. In an attempt to lessen the interference from visible surface defects, experiments have been carried out using a coil of much larger internal diameter than the bar, but in such conditions sensitivity to internal defects is also seriously reduced.

2. INSPECTION FOR SURFACE DEFECTS

A careful visual inspection is necessarily carried out on all finished products, and it is also made at many intermediate stages to ensure, as far as is practicable, that only sound material moves forward from one operation to another.

While machined or hot-rolled surfaces can in some cases be inspected without special preparation, a more detailed inspection can be made after cleaning of the surface by bright-annealing or by shot-blasting and/or pickling. Shot-blasting alone is useful in revealing deep cracks, but there is a tendency for smaller cracks to be thus blended over or partly filled with metal debris. Although it is a cheap and quick method of removing oxide from a cast or hot-rolled surface, blasting suffers from the disadvantage, compared with a pickling operation, that the grain-size is not revealed. This latter limitation applies also to bright-annealing, which, however, is a useful inter-stage operation, since imperfections under the oxide skin are revealed. This treatment is found to be particularly useful in the production of nickel coinage strip, when the hot-rolled strip bar is annealed before cold rolling in an atmosphere of partially burnt town gas. Hot-rolling defects are revealed and can be removed by a “bobbing” operation.

Pickling is an unpleasant operation, but it provides probably the best type of surface for inspection, and is used as the final or near-final operation for the nickel–chromium alloys of groups (2) and (3).

For sheet of these alloys, three methods of pickling are used:

(a) After hot-rolling and annealing, the sheets are first immersed for 4–8 hr. in alkaline potassium permanganate at 90° C., followed by not less than 1 hr. in

a sodium nitrate-sulphuric acid solution at 70° C. The advantage of the alkaline pickle lies in the oxidation and solution of the chromium oxide, with loosening of the associated nickel oxide. Such treatment has no effect on the underlying metal; over-pickling, with resultant loss of metal, is thus impossible.

(b) Finished cold-rolled sheet, after annealing, is pickled in an aqueous solution containing 5% hydrofluoric acid with 20% nitric acid, used at a temperature not above 35° C. Containers for this very corrosive pickle are wooden vats lined with sheets of polythene.

(c) A more rapid treatment, alternative to either of the foregoing methods, is to immerse the sheet in molten caustic soda containing 10% sodium nitrate, at 500° C. for about 10 min. After washing, the sheet is pickled for another 10 min. in the nitric-hydrofluoric acid mixture described in (b).

The rate of cooling of alloys of group (3) from the annealing temperature is important in its effects on response to pickling. Slow cooling results in susceptibility to intergranular corrosion when the sheets are subsequently pickled in the very corrosive nitric-hydrofluoric acid. A severe case of this type of attack is illustrated in Fig. 1 (Plate XXXVI), the attack being clearly revealed by the rough surface of an Erichsen impression; Fig. 2 (Plate XXXVI) shows a typical cross-section of heavily attacked material. Such corrosion never occurs in the caustic soda-permanganate pickle, since only the oxide is dissolved and the metal itself is unaffected. The susceptibility of these alloys to intercrystalline pickle attack increases with both time and temperature of annealing, but it can be avoided by quenching in cold water after the annealing treatment. Material known to be in a susceptible condition may be re-conditioned by heating to a temp. of 950° C. for approximately 10 min., after which the rate of cooling is unimportant. It must, however, be emphasized that it is impossible to re-condition material which has been subjected to pickling in the nitric-hydrofluoric acid while in the susceptible condition and has suffered intergranular attack. The length of time required for adequate pickling is dependent upon the condition of the material, but the treatment should in no case be longer than 4 hr.

After pickling, the surface of sheet and strip is examined for blisters, intergranular corrosion or oxidation, bobbing cracks (due to local overheating in bobbing the hot-rolled product), pits, poor surface due to contact with oil or other fluids, &c.

For machined bar material of the same alloys, a useful inter-stage and final inspection operation is electrolytic etching; this process is used mainly to reveal residual defects such as fine cracks present after machining, or stringers of inclusions, particularly of titanium cyanonitride in titanium-bearing alloys. The method is also useful in the inspection of hot-rolled rod, in which case it is desirable to remove the scale by shot-blasting before etching; otherwise severe pickling might occur before all the scale was removed.

The electrolyte consists of equal proportions of

commercial hydrochloric acid and water and is used cold. A 2-V. rectifier supplies up to 500 amp. to each vat and a current density of approximately 1 amp./in.² is maintained for about 2 min., the bars being made the anode. The etched rods are washed in running water, allowed to drain, and inspected.

In the latter stages of manufacture, bars and sections of these alloys are examined for the presence of stringers of inclusions or residual pipe. The ends of the bars are etched in boiling hydrochloric acid until the crystal size is just revealed. The acid is of the "constant-boiling" composition, and the time of pickling is about 15-20 min. Pits on the bar ends, a very serious case of which is shown in Fig. 3 (Plate XXXVI), indicate the presence of stringers. Figs. 4 and 5 (Plate XXXVII) illustrate sections through such stringers, before and after etching.

VI.—PROCESS TESTING

In a number of cases it is necessary that nickel alloys, in addition to having the specific physical or mechanical properties required for a particular application, shall be capable of being processed by particular manufacturing operations. To ensure such suitability, special process tests have been devised, some of which are described below.

1. WELDING TEST OF NICKEL-CHROMIUM VALVE-COATING ALLOY

A special variety of 80 : 20 nickel-chromium alloy is used for welded protective coating of aero-engine valve heads, and on such material a routine welding test is carried out on a sample from each heat.

The test consists of deposition of a bead from each sample, on to the surface of a 12 × 6-in. mild-steel plate which has been shot-blasted to remove all scale, rust, &c. Using an oxy-acetylene torch (with the flame correctly adjusted for this type of welding), the steel plate is heated locally until the surface begins to "sweat". The end of the $\frac{3}{16}$ -in.-dia. welding-wire sample is then melted on to the steel, depositing a bead 2-3 in. long. As a test criterion, note is taken of the ease with which the end of the wire is melted off, the fluidity of the molten metal over the surface of the steel plate, the formation and tenacity of the oxide skin on the molten surface of the deposit, and any tendency to sparking.

2. WELDING TEST OF NICKEL-CHROMIUM-IRON ALLOY FOR HEATER SHEATHS

In electric cookers a nickel-chromium-iron alloy containing chromium 15 and iron 7% is used to sheath heating elements in which the element is insulated from the sheath by a packing of magnesia. The tubing for the sheath is about $\frac{3}{8}$ in. in dia. and is produced by drawing strip through dies and welding the gap by the atomic-hydrogen process.

From each cast of alloy to be allocated to this pro-

duct, a pilot ingot is processed to strip, which is drawn to shape and welded by the production procedure.

After examination of the tubes for correct depth of penetration of the weld, they are cut to 12-in. lengths, annealed at 1050° C. for 10 min, and air-cooled. They are then scribed with a series of $\frac{3}{4}$ -in. gauge-marks, and pulled to fracture; elongation over the gauge-length embracing the fracture is measured. The suitability of the material is assessed on the quality of the weld and the elongation values obtained.

3. SPIRALLING TEST FOR WIRE

Every coil or reel of heater-gauge nickel-chromium wire is subjected to a spiralling test, which consists essentially of forming about 9 in. of close spiral on a $\frac{3}{16}$ - or $\frac{3}{32}$ -in.-dia. mandrel. The mandrel is motor-driven, and the wire is fed on to it by hand from the reel, care being taken to see that each turn touches the next. If the spiral runs back on itself, it is rejected and another one must be formed.

The spiral is removed from the mandrel and stretched by hand; it is rated as satisfactory only if the turns are uniformly spaced, since any unevenness of spacing would lead to irregular temperatures and premature failure of the wire in a resistance-heater element. Fig. 6 (Plate XXXVII) illustrates an unstretched and a uniformly and an unevenly stretched spiral. The usual cause of poor spiralling is uneven annealing or cracked wire.

4. TEST FOR GAS-FREE NICKEL

Freedom from gas in wire and strip is necessary for certain applications, such as anode plates and grids in radio valves. Gas content is determined on a specimen from each coil or reel of such material, by observation of the gas evolved at 800° C. A length of about 4 in. of the wire is degassed with trichloroethylene. A glass tube, 2 in. long and of about the same internal diameter as the wire and having one end closed, is then placed on the end of the wire, which is revolved in a flame so that the glass tube collapses about it. This portion is then heated at 800° C. for 3 min., allowed to cool, and examined. With gas-free nickel very few gas bubbles are seen, but with gassy nickel many small bubbles are formed in the glass. Examples of such tests are illustrated in Fig. 7 (Plate XXXVII).

5. PLATING TEST FOR NICKEL ANODES

For the hot-rolled oval-section nickel which is used for electroplating anodes, a pilot plating check-test is employed. A 6-in. length of bar is cut, a hook is fitted, and the test anode is shot-blasted. It is then weighed, enclosed in a canvas bag, and hung in the plating bath between two cathodes. The electrolyte consists of: nickel sulphate 40, nickel chloride 5, and boric acid 4 oz./gal. The pH, which is automatically recorded, is maintained at 5.3 by small additions of

hydrochloric acid, and the temperature is thermostatically controlled at 48°–50° C. The electrolyte is continually circulated and filtered. Plating is carried out under fixed conditions of current and time. The quality of the nickel is assessed by the anode efficiency, and by the amount and character of the sludge deposited, which consists mainly of nickel oxide and metallic nickel. The proportion of metal in the sludge, and the shape of the metallic grains, are also relevant factors in determining the quality of the anode.

VII.—PHYSICAL AND MECHANICAL PROPERTIES

A wide variety of special routine tests of physical and mechanical properties is applied to nickel alloys. Some are carried out to satisfy official specification requirements; others to meet the needs of particular customers. The more important of these tests are dealt with below.

1. MAGNETIC ALLOYS

The properties of magnetic alloys depend on major chemical composition, impurities, segregation, method of fabrication, and heat-treatment. There are, however, two distinct groups of properties which may be classified respectively as structure-insensitive and structure-sensitive.

Structure-insensitive properties include saturation magnetization and Curie point, and accordingly, where the shape of the magnetic intensity/temperature curve is the main interest, as in magnetic-compensation materials such as 30 : 70 nickel-iron and 70 : 30 nickel-copper alloys, the production problems are concerned mainly with close control of composition. Checking of the induction/temperature curve is best carried out with a Sucksmith ring balance,¹¹ although the ballistic method can also be used.

Structure-sensitive properties, such as permeability, coercive force, linear magnetostriction, &c., are controlled mainly by empirical methods based on the determination of a part or the whole of the hysteresis loop. This may be obtained at any desired frequency by means of a cathode-ray oscilloscope or, under D.C. conditions, by the ballistic method. The permeability of alloys for use at high frequency, such as the silicon-iron and nickel-iron alloys, can be obtained by using an A.C. bridge to measure the inductance of a toroid wound on a suitable number of annealed rings cut from sheet.

2. CONTROLLED-EXPANSION ALLOYS

Nickel-iron and nickel-cobalt-iron low-expansion alloys find applications for thermostats, for standard measuring tapes and gauges, and for sealing into glass to form vacuum-tight leads into electronic tubes of all types. Most users of these alloys specify close ranges of thermal-expansion coefficient and, since melting variables and varying amounts of deoxidizers and

impurities can exert considerable effect on the expansion properties, control tests have to be made on every heat of such alloys. The usual procedure is to hold the production ingot in store until expansion tests on a pilot sample show that the heat complies with the relevant specification. The pilot ingot is forged and rolled into rod of a convenient size (about $\frac{3}{8}$ in. dia.), from which is machined a test-piece of a form suitable for the measuring equipment. After annealing the test-piece to remove all cold work, an expansion/temperature curve is plotted during slow heating and cooling of the specimen over the specified temperature range. An alternative method is to compare the expansion of the specimen with that of a known standard, in a differential dilatometer.

Some users of the alloys for glass-to-metal seals carry out further tests by making test seals between a small sample of the alloy and the glass with which it is to be used. These seals are then examined, under polarized light, for the presence of residual stresses, and only if the stresses are below a specified value is the material accepted for use.

3. ELECTRICAL-RESISTANCE ALLOYS

All materials sold, in the form of wire and tape, for electrical-resistance purposes are checked for resistance at the final size. This is chiefly because the dimensional tolerance, for example on the diameter of wire of a given nominal gauge, allows considerable variation of the resistance per unit length of the wire. The permissible variations of resistance from the nominal value, and the uniformity of resistance, are normally in conformity with the requirements of British Standards 115 and 1117. Each reel or coil is individually tested, using a modified Wheatstone bridge.

Resistance measurements form a very useful check on the material of a wire. For this purpose it is essential that wires being checked shall be in a given metallurgical condition, since resistivity varies according to the condition of the wire, e.g. the specific resistivity of 80 : 20 nickel-chromium is 10% lower in the cold-worked state than in the annealed condition. Rate of cooling from annealing also has an effect; rapid cooling produces a resistivity about 5% lower than that resulting from slow cooling. A description and explanation of these effects has recently been given by Taylor and Hinton.¹² For the identification of materials by resistivity measurements, it is, of course, essential that the dimensions of the material shall be determined with an accuracy comparable to that used for the resistance measurements. Wire diameters and ovality are therefore checked with a micrometer reading to 0.00005 in.

4. THERMOELECTRIC PROPERTIES

Nickel-copper alloys are used, *inter alia*, as thermocouple wires in conjunction with pure copper, and the following test procedure is adopted in the production of material for this purpose. A pilot ingot is pro-

cessed to wire, and the e.m.f. of a couple formed between this wire and electrolytic copper is checked by conventional methods for temperature differences of 0°–100° C. (standard e.m.f., 4.26 mV.) and 0°–327.4° C., the melting point of lead (standard e.m.f., 16.226 mV.). The results of these tests determine whether the material is suitable for thermoelectric applications. The bulk material, after drawing to wire, is again checked over the temperature range 0°–100° C. by comparison with a standard sample of the same type of nickel-copper alloy.

5. LIFE TESTING OF WIRES FOR ELECTRICAL HEATING

The test applied to 80 : 20 nickel-chromium wire for electrical-heating elements follows essentially the A.S.T.M. test B76-39, in which wires of 20 S.W.G. are suspended vertically in a draught-free chamber, heated electrically to a temperature set by an optical pyrometer, and the heating current switched on and off at 2-min. intervals. The life of the wire depends to a major extent on the degree of adherence of the scale to the wire, for when a portion of scale flakes from the wire a hot spot forms, which is followed by an accelerated rate of oxidation at that point, and ultimate burn-out. The mechanism of burn-out has been investigated by Betteridge.¹³

The standard temperature for the test of nickel-chromium wires is given in the A.S.T.M. Specification as 1177° C. (2150° F.), but in view of recent improvements in the quality of wire effected by modification of the content of minor elements, e.g. calcium, cerium, zirconium, and silicon, the test temperature has been raised to 1232° C. (2250° F.) in order to prevent the testing time being unduly prolonged. The progress made in this field over the last 20 years is indicated by the typical results given in Table III. The test is

TABLE III.—*Improvement in Quality of Nickel-Chromium Wire as Gauged by Accelerated Life Test.*

Year	Test Temperature, to Give Life of 100–200 hr.		Year	Test Temperature, to Give Life of 100–200 hr.	
	°C.	°F.		°C.	°F.
1930–36	1066	1950	1939–53	1177	2150
1936–39	1120	2050	1953	1232	2250

carried out in this manner on all heats of the alloy intended for intermittent use at elevated temperatures. For continuous operation at similar temperatures the accelerated alternate heating and cooling test is not regarded as relevant.

6. CREEP TESTING

The major test used for control of the quality of the creep-resisting alloys of group (3) is a pilot creep test of about 100 hours' duration. The specifications to which these alloys are supplied are usually D.T.D.

specifications (e.g. D.T.D. 725, 736, and 747). The tests are normally carried out on material from small ingots which are processed to bar in advance of the bulk material. The pilot ingot is forged to bar about $\frac{5}{8}$ in. in dia., from which test-bar lengths are cut, and heat-treated by the specified procedure. These bars are machined to test-pieces with $\frac{1}{2}$ in. Whitworth screwed ends, and a gauge-length nominally $2\frac{1}{4}$ in. long, and 0.252 in. in dia. Testing is carried out in a relatively simple apparatus, which has been described by Weaver.¹⁴ Temperature is controlled by an expansion-thermostat, and strain measurements are made by a dial-gauge operating on the lever of the machine. The specification usually includes three criteria: secondary-creep rate, time to the onset of accelerating or tertiary creep, and time to fracture. Strain measurements are recorded at suitable intervals during the test, and a strain/time creep curve is plotted, from which values of the secondary-creep rate and of the time to the onset of tertiary creep are derived. The time to fracture is accurately recorded by an electric clock and counter system, the circuit of which is interrupted by the rupture of the bar. In order to confirm that the results on pilot-test bars are representative of the material in its final form, similar tests are carried out from time to time on miniature test-bars cut from components such as turbine blades.

VIII.—PACKING AND DESPATCH

The packing of material for despatch demands care to ensure that the quality is maintained in transit to the customer. For heavier-section material, such as bar, this usually involves no more than bundling and labelling of consignments, although for export orders the bar is packed in wooden cases. Much greater care needs to be taken of sheet material, particularly of cold-rolled products having a high surface finish. These are interleaved with paper and packed in a wrapping of corrugated paper in a wooden case, care being taken that the case is close-fitting, to prevent looseness of the sheets leading to damage of the edges. Hot-rolled sheet of the thinner gauges is also packed in wooden cases, but sheet over $\frac{1}{4}$ in. thick is covered only at the edges with corrugated paper and secured with metal bands in batches not exceeding 10 cwt. in weight.

The most interesting aspect of packaging is the procedure adopted for the handling of wire, which again is very dependent on the gauge. For sizes above 13 S.W.G. the wire is despatched in coils, which are paper-wrapped for the home trade, but packed in wooden cases for export. Wire between 13 and 18 S.W.G. is supplied either in coil form or on wooden drums holding up to 28 lb. Wire of 18–43 S.W.G. is wound on wooden spools of varying sizes holding between $\frac{1}{4}$ and 7 lb., while gauges of 44 S.W.G. and finer are supplied on aluminium spools holding up to 4 oz. The latter spools of wire are enclosed in transparent plastic cases for despatch.

ACKNOWLEDGEMENTS

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REFERENCES

1. Richard M. Bozorth, "Ferromagnetism", p. 146. 1941: New York (D. Van Nostrand Co. Inc.); London (Macmillan and Co., Ltd.).
2. W. R. Barclay, G. A. V. Russell, and H. Williamson, *J. Inst. Metals*, 1932, **49**, 391.
3. L. H. Martin and L. O. Bieber, *Non-Ferrous Rolling Practice (A.I.M.M.E. Symposium)*, **1948**, 15.
4. M. P. Buck and N. C. Britz, *ibid.*, 33.
5. M. P. Buck and N. C. Britz, *Rod and Wire Production Practice (A.I.M.M.E. Symposium)*, **1949**, 23.
6. W. A. Dickinson and H. F. Hendershot, *Tube Producing Practice (A.I.M.M.E. Symposium)*, **1951**, 83.
7. J. Strauss, *Blast Furnace and Steel Plant*, 1952, **40**, 1184.
8. J. Sejournet, *Engineering*, 1954, **177**, (4602), 463.
9. H. J. Hartley and E. J. Bradbury, *J. Inst. Metals*, 1951–52, **80**, 297.
10. British Patent No. **567,766**.
11. "Eddy-Current Instruments for Use in the Field of Non-Destructive Testing" (B.I.O.S. Final Report No. 1791) [1948]. London (H.M. Stationery Office).
12. W. Sucksmith, *Proc. Roy. Soc.*, 1939, [A], **170**, 551.
13. A. Taylor and K. G. Hinton, *J. Inst. Metals*, 1952–53, **81**, 169.
14. W. Betteridge, *4th Internat. Congr. Indust. Heating (Paris)*, **1952** (Paper No. 18).
15. C. W. Weaver, *Bull. Inst. Metals*, 1953, **1**, (18), 168.

PSEUDO-BINARY PHASE SECTIONS BETWEEN LAVES 1595 PHASES IN TERNARY ALLOYS OF URANIUM*

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SYNOPSIS

The phase boundaries at 700° and 900° C. have been determined in the pseudo-binary systems $\text{UMn}_2\text{--UNi}_2$, $\text{UFe}_2\text{--UNi}_2$, and $\text{UCo}_2\text{--UNi}_2$. The *C15* structures of UMn_2 , UFe_2 , and UCo_2 are progressively replaced first by an intermediate hexagonal *C36* structure and then by the hexagonal *C14* structure of UNi_2 . At 900° C. the ranges of the two terminal solid solutions, based respectively on the *C15* and *C14* structures, become rather more restricted on passing from manganese to iron to cobalt. Conversely, the range of the intermediate solution with the *C36* structure is widened on passing from manganese to iron to cobalt. The phase boundaries differ only slightly at 700° C. It is concluded that the positions of the phase boundaries in these sections cannot be explained by simple considerations of either size-factor relationships or the electron:atom ratios, regarded separately.

I.—INTRODUCTION

THE so-called "Laves phases" are close-packed compounds of approximate formula AB_2 , crystallizing in one of the three structural types: ¹

C14 hexagonal, MgZn_2 -type, with packing *ABABAB* . . .

C15 cubic, MgCu_2 -type, with packing *ABCABC* . . .

C36 hexagonal, MgNi_2 -type, with packing *ABACAB* . . .

Ideally the ratio, d_A/d_B , of the interatomic distances in the pure components should equal 1.225. In fact, it varies from about 1.1 to 1.6.

Most of the original work on the relationship between the *C14*, *C15*, and *C36* structures was carried out by Laves and his collaborators ² with magnesium as the *A* element. Progressive replacement of copper in MgCu_2 and zinc in MgZn_2 by elements of lower and higher valency showed that the sequence of structural changes:



generally occurred as the electron:atom ratio increased from:

$$<0.92 \longrightarrow (1.08\text{--}1.76) \longrightarrow (1.81\text{--}1.92) \longrightarrow >2.0$$

provided that the transitional elements were allocated valencies close to zero.

More complex structures have been observed in some ternary systems. For example, in the pseudo-binary section extending from MgZn_2 towards the composition MgAg_2 , the phases with the *C14* and *C36* structures are separated by several complex phases, one of which has a hexagonal structure with a *c* parameter four times that of the *C36* structure.³

More recently, Berry and Raynor ⁴ have listed the

known *C14* and *C15* Laves compounds and have shown that, in many cases, their formation depends on a size-factor relationship, the *C15* structure being more likely to occur as the ratio of interatomic distances deviates from the ideal value. The electron:atom ratios become much more important when the atomic-size factors are very favourable, as in the magnesium alloys studied by Laves *et al.* Kuo ⁵ examined the Laves phases formed by titanium, tantalum, niobium, and zirconium with the transitional metals of the First Long Period from vanadium to nickel, and showed that with transitional metals of successively higher atomic number the sequence of structures is:



He found that if the *B* element were replaced by two elements *B'* and *B''* of the same Period, lying on opposite sides of *B*, a ternary Laves phase often occurs, even though in some cases binary Laves phases AB'_2 and AB''_2 do not exist.

Uranium is known to form Laves phases with the transition metals of the First Long Period. Of these UMn_2 , UFe_2 , and UCo_2 have the cubic *C15* structure, whilst UNi_2 has the hexagonal *C14* structure.⁶ The phase UCr_2 does not exist.⁷ From manganese to nickel the sequence of structures $C15 \longrightarrow C14$ is observed. The further change $C14 \longrightarrow C15$ beyond nickel, comparable with Kuo's observations, does not occur; however, the uranium-copper system includes a phase UCu_5 with a structure similar to that of the *C15* Laves phase.⁸

The phase relationships in the pseudo-binary sections $\text{UNi}_2\text{--UMn}_2$, $\text{UNi}_2\text{--UFe}_2$, and $\text{UNi}_2\text{--UCo}_2$ have been studied by the present authors in order to compare the alloying behaviour of the transitional elements (including uranium) and the structures

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formed, with those of the magnesium and other Laves phases.

II.—EXPERIMENTAL PROCEDURE

1. MATERIALS AND PREPARATION OF ALLOYS

The uranium was aluminium-free, but contained some oxide impurity. Electrolytic flake manganese was used after surface cleaning. The other components were high-purity electrolytic iron and nickel and remelted cobalt sponge.

The uranium-nickel-iron and uranium-nickel-cobalt alloys were prepared in an argon-arc furnace as 50-g. buttons. Volatilization of manganese precluded the use of an arc furnace for the uranium-nickel-manganese alloys. The uranium and nickel were pre-alloyed in the arc furnace, and the resulting button remelted with the manganese in a beryllia crucible under an atmosphere of specially purified argon. These alloys were cast in the form of a rod about 12 mm. in dia.

The alloys were all extremely brittle and usually fractured during cooling in the furnace.

2. HEAT-TREATMENT

Specimens of alloy in thin-walled alumina crucibles were sealed under vacuum in silica tubes and placed in a Nimonic block in a vertical furnace controlled to $\pm 2^\circ\text{C}$. for either: (a) 1 week at 900°C . or (b) 1 week at 900°C ., followed by 4 weeks at 700°C . Doubling the time at 700°C . and quadrupling the time at 900°C . had no effect on the structures. The specimens were quenched into cold water, the silica tubes breaking immediately.

3. METALLOGRAPHIC TECHNIQUE

The micro-specimens were polished by normal methods, using γ -alumina as the final abrasive. When examined under polarized light the cubic C15 could be distinguished from the hexagonal C14 or C36 structure. The most satisfactory etching reagent was a solution containing 10 g. of oxalic acid in 45 c.c. water and 45 c.c. glycerol, used electrolytically. At 10 V. some relief occurred; further etching at 5–6 V. stained the surface brown, the constituent richer in nickel being always a deeper brown. A 10% oxalic acid solution in water was also used with similar results, but its action was more rapid and less controllable.

4. X-RAY TECHNIQUE

The alloy was broken up in an agate mortar until a clean piece of metal from the centre of the ingot was obtained. A small fragment of this was ground into a fine powder under alcohol to minimize oxidation. Rods suitable for X-ray examination were prepared, using 7 parts of gum tragacanth as a diluent. Negligible cold work was introduced into the specimens

during the crushing operation, and sharp lines were obtained on the powder patterns without further heat-treatment. Lines due to uranium oxides were never observed.

In case any ductile phases were present, X-ray photographs of a number of micro-specimens were taken with the specimen oscillated about a vertical line in its own plane. The films obtained in this way were not very satisfactory owing to the large grain-size of the solid specimen, but they showed no lines other than those present on the equivalent powder pattern.

The X-ray powder photographs were taken with a 9-cm. Debye-Scherrer camera. Cobalt characteristic radiation from a self-rectifying gas X-ray tube was used with an exposure time of 8–10 m.amp.-hr. at 40 kV. peak. The disappearing-phase method was used to determine the extent of the various phase fields. The homogeneity of the ingots was tested by making powder specimens from different samples and comparing the Debye-Scherrer patterns. Lattice-spacing determinations in pseudo-binary systems are subject to enhanced scatter owing to the possibility of variation in composition on either side of the pseudo-binary line. It was considered, however, that a plot of the parameter values against composition would be unlikely to provide greater accuracy in fixing the phase boundaries.

Lattice parameters of cubic phases were determined by standard extrapolation.⁹ For hexagonal phases a modified form was used; the axial ratio was assessed from a Bunn chart and the a parameter extrapolated, as for cubic phases. Lines with low l index lie on this extrapolation. The axial ratio was re-assessed from the nature of the scatter of points with high l index and the extrapolation re-plotted to obtain the best fit. When a trace of cubic phase was also present, the extrapolation suggested by Bacon¹⁰ was used.

Lattice parameters were not corrected for variations in the ambient temperature of up to $\pm 3^\circ\text{C}$., since thermal-expansion data were not available.

5. ANALYSIS

Analyses were carried out on a specimen taken from a region close to the X-ray sample. This was electropolished to remove the surface layers depleted in uranium during heat-treatment.

The agreement between intended and actual compositions was usually within 0.5% in the U-Ni-Fe and U-Ni-Co alloys, but the difference was occasionally as much as 2% in the U-Ni-Mn alloys, from which a variable amount of manganese was lost. The uranium content was usually within $\pm 0.5\%$ of the intended figure of 33.3 at.-%.

III.—EXPERIMENTAL RESULTS

The pseudo-binary phase sections reproduced in Fig. 1 are based on metallographic and X-ray examinations which were in good agreement. Each section

contained three single-phase regions at both 900° and 700° C., namely, the terminal solid solution based on UNi_2 , with the $C14$ structure; the terminal solid solution based on UMn_2 , UFe_2 , or UCo_2 , with the

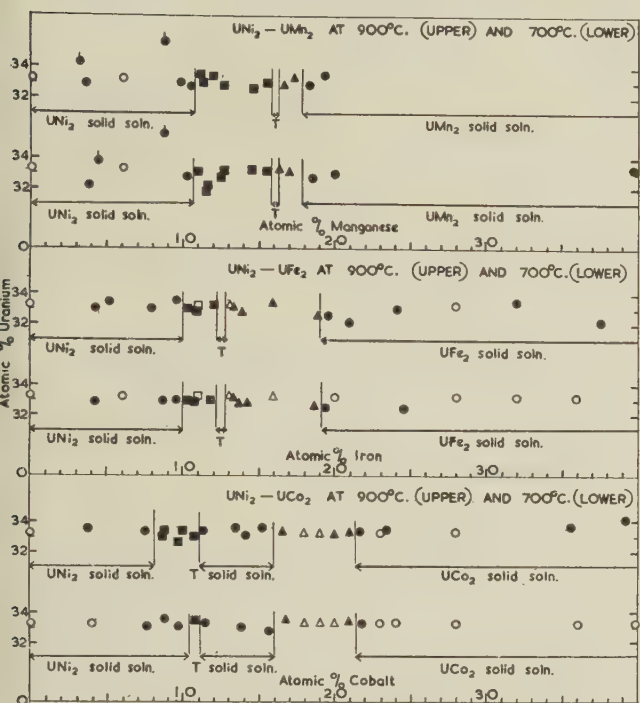


FIG. 1.—Phase Boundaries at 900° and 700° C. in Pseudo-Binary Sections $\text{UNi}_2\text{--UMn}_2$, $\text{UNi}_2\text{--UFe}_2$, and $\text{UNi}_2\text{--UCo}_2$. The closed symbols represent analysed and the open symbols unanalysed alloys.

KEY.

- Single Laves phase.
- " " " + liquid.
- Bi-phase ($\text{UNi}_2 + T$).
- ▲ " ($T + \text{UM}_2$).

$C15$ structure; an intermediate solid solution, T , with the $C36$ structure. The estimated solubility limits are set out in Table I.

TABLE I.—Composition of Solubility Limits in $\text{UNi}_2\text{--UM}_2$ Pseudo-Binary Sections.

M = Manganese, iron, or cobalt.

Boundary	900° C.		700° C.	
	Ni, at.-%	M , at.-%	Ni, at.-%	M , at.-%
$\text{UNi}_2/(\text{UNi}_2 + T_{\text{Mn}})$	55.9	10.7	55.9	10.6
$T_{\text{Mn}}/(\text{UNi}_2 + T_{\text{Mn}})$	50.9	15.8	50.9	15.8
$T_{\text{Mn}}/(T_{\text{Mn}} + \text{UMn}_2)$	50.5	16.2	50.5	16.2
$\text{UMn}_2/(T_{\text{Mn}} + \text{UMn}_2)$	48.9	17.8	48.9	17.8
$\text{UNi}_2/(\text{UNi}_2 + T_{\text{Fe}})$	56.9	9.8	56.7	10.0
$T_{\text{Fe}}/(\text{UNi}_2 + T_{\text{Fe}})$	54.5	12.2	54.5	12.2
$T_{\text{Fe}}/(T_{\text{Fe}} + \text{UFe}_2)$	53.9	12.8	53.9	12.8
$\text{UFe}_2/(T_{\text{Fe}} + \text{UFe}_2)$	47.7	19.9	47.6	19.1
$\text{UNi}_2/(\text{UNi}_2 + T_{\text{Co}})$	58.5	8.2	56.3	10.4
$T_{\text{Co}}/(\text{UNi}_2 + T_{\text{Co}})$	55.6	11.1	55.6	11.1
$T_{\text{Co}}/(T_{\text{Co}} + \text{UCo}_2)$	50.7	16.0	50.7	16.0
$\text{UCo}_2/(T_{\text{Co}} + \text{UCo}_2)$	45.3	21.4	45.2	21.5

1. X-RAY IDENTIFICATION OF PHASES

Fig. 2 (Plate XXXVIII) shows films of the hexagonal phase, UNi_2 ($C14$ structure); cubic phase, UCo_2 ($C15$ structure); and the intermediate hexagonal phase, T ($C36$ structure).

The similarity between the film of the $C14$ structure and that of the $C36$ structure is apparent. All the lines of the $C36$ film could be indexed on a cell of approximately twice the axial ratio of the $C14$ cell. Since the axial ratio of the $C36$ cell was not exactly twice that of the $C14$ phase, the relative positions of some of the lines changed, particularly those with high l indices; e.g. the relative separation of the $C36$ lines (220) and (1, 0, 12) (2, 0, 10) differed from the separation of the equivalent lines (220) and (106) (205) of the $C14$ structure. This relative separation, though small, provided a useful criterion for establishing the presence of a second phase whose faint diffraction lines might be masked.

When both $C14$ and intermediate phases were present, some of the lines were broadened owing to this inexact overlap of corresponding lines. Fig. 2 (ii) shows line (414) of the $C36$ structure lying almost, but not exactly, on line (412) of the $C14$ structure, which is also present in this alloy.

In the $\text{UFe}_2\text{--UNi}_2$ and $\text{UCo}_2\text{--UNi}_2$ systems the observed line intensities of the T phase were in accordance with those calculated for the $C36$ structure. In the $\text{UMn}_2\text{--UNi}_2$ intermediate phase, the extra lines of the $C36$ structure were visible, but reduced in intensity.¹¹

An additional Debye-Scherrer pattern was observed in approximately the centre of the T field of the $\text{UFe}_2\text{--UNi}_2$ and $\text{UCo}_2\text{--UNi}_2$ systems. This pattern was the same for both systems and was similar to that of the $C36$ -type structure. Single-crystal work showed that the structure was of hexagonal symmetry with a large c spacing¹¹ and thus bore a similarity to the intermediate phase found by Witte³ in the $\text{MgZn}_2 \rightarrow \text{MgAg}_2$ section. Remelting the buttons giving this new structure yielded the same pattern and chemical analysis showed them to be of the correct composition. It did not prove possible to reproduce this structure at will; further melts of the same composition yielded the T pattern irrespective of heat-treatment.

2. METALLOGRAPHIC IDENTIFICATION OF PHASES

Metallographic examination could distinguish satisfactorily between two phases in the bi-phase regions, that richer in nickel being stained a darker brown than the other (Fig. 3, Plate XXXIX). The optical anisotropy of the hexagonal phases made it possible to distinguish them from the cubic UMn_2 , UFe_2 , and UCo_2 phases by the use of polarized light. Figs. 5 and 6 (Plate XXXIX) show how the grain structure of the UNi_2 solid solution was revealed. Several other phases were observed in small quantities. One of these, believed to be an oxide or nitride, was derived from the uranium. In uranium it appeared as small

regular particles, usually blue-grey in colour. After alloying, pink-grey dendrites were observed, and in the worst examples these had a core of the regular particles observed in uranium (Fig. 4, Plate XXXIX), giving the appearance of an incomplete peritectic reaction.

During heat-treatment loss of uranium occurred from the surface and resulted in the introduction of layers of the same phases as were occasionally observed in small amounts in alloys containing less than 33 at.-% uranium. One of these, which was optically isotropic, appeared as narrow bands within UNi_2 or T , especially near the outside. The other, strongly anisotropic, took the form of a white precipitate at grain boundaries and a Widmanstätten structure on annealing alloys containing less than 33 at.-% uranium at 700° C. (Fig. 5, Plate XXXIX). This occurred in the binary alloy of nominal composition UNi_2 , and the precipitate is believed to be based on the X phase of the U-Ni system.¹² These phases never occurred in any but very small quantities and have been ignored in drawing the phase sections. In the $\text{UNi}_2\text{-UFe}_2$ and $\text{UNi}_2\text{-UCo}_2$ section in alloys containing T and UNi_2 , and in T at the nickel-rich limit, signs of decomposition were visible in the T phase. This could be observed only with difficulty in the single-phase T alloys. In bi-phase alloys the product appeared to consist of plates of UNi_2 , which were related to adjacent particles of UNi_2 (Figs. 7 and 8, Plate XXXIX). The reaction occurred both on quenching and on slow cooling (at 2° C./min.) from 900° and 700° C. and appeared to represent precipitation during cooling. The change in solubility of cobalt in UNi_2 between 900° and 700° C. may be responsible, and this suggests that a similar change in solubility may occur in the $\text{UNi}_2\text{-UFe}_2$ system below 700° C.

On annealing at 700° C. there was a little precipitation of T in a Widmanstätten manner in UFe_2 and UCo_2 in bi-phase alloys, suggesting a decreasing solubility of nickel in UFe_2 and UCo_2 with falling temperature. However, on the basis of analyses of alloys containing nominally 18 at.-% iron (UFe_2 and T) and 19 at.-% iron (UFe_2 only) at 900° and 700° C., the change in solubility must be very small, i.e. less than 0.5 at.-% iron.

3. LATTICE-PARAMETER DETERMINATIONS

The parameters of alloys with the C14, C36, and C15 structures are given in Tables II-IV, respectively. These were determined at approximately 20° C., using cobalt radiation of a wave-length of 1.78529 kX units for $\text{CoK}\alpha_1$ and of 1.78919 kX units for $\text{CoK}\alpha_2$. Tables II-IV also contain the interatomic distances of like atoms.

In the case of C36 and C15 and in the C14 single-phase fields, the results for alloys quenched from 900° and 700° C. lay on a smooth curve (Fig. 9). A number of points obtained from alloys quenched from 1000° C. lay off this curve, and no satisfactory explanation for

TABLE II.—*Lattice Spacings and Interatomic Distances for Alloys with C14 Structure, After Quenching from 900° C.*

Composition	Lattice Spacing, kX			Interatomic Distance, kX *	
	<i>a</i>	<i>c</i>	<i>c/a</i>	<i>d_{M-M}</i>	<i>d_{U-U}</i>
UNi_2	4.949 ₅	8.228 ₅	1.662 ₅	2.474 ₈ 2.504 ₄	3.192 ₇ 3.002 ₅
UNi_2 (containing 12% UFe_2)	4.951 ₃	8.229 ₁	1.662 ₀	2.476 ₇ 2.504 ₇	3.192 ₉ 3.003 ₅
UNi_2 (containing 12% UCo_2)	4.946 ₅	8.221 ₁	1.662 ₀	2.473 ₂ 2.502 ₄	3.189 ₈ 3.000 ₆
UNi_2 (ref. 5)	4.956	8.235	1.660

* Unless the axial ratio is exactly $\sqrt{8/3}$, neither the U atoms nor the M atoms are all equidistant; and two M-M and two U-U distances are involved:

$$d_{M-M} = -3xa \text{ or } \sqrt{(3x^2a^2 + C^2/16)}, \text{ where } x = -\frac{1}{6}$$

$$d_{U-U} = C(\frac{1}{2} - 2z) \text{ or } \sqrt{[a^2/3 + (2cz)^2]}, \text{ where } z = 0.056$$

TABLE III.—*Lattice Spacings and Interatomic Distances for Alloys with C36 Structure, After Quenching from 900° C.*

Composition	Lattice Spacing, kX			Interatomic Distance, kX *	
	<i>a</i>	<i>c</i>	<i>c/a</i>	<i>d_{M-M}</i>	<i>d_{U-U}</i>
T_{Mn} (saturated with UNi_2)	4.976 ₀	16.420 ₁	3.300 ₀	2.48 ₈	3.07 ₉
T_{Fe} (saturated with UNi_2)	4.961 ₈	16.390 ₈	3.303 ₄	2.48 ₁	3.07 ₃
T_{Fe} (saturated with UFe_2)	4.963 ₈	16.397 ₀	3.303 ₃	2.48 ₂	3.07 ₄
T_{Co} (saturated with UNi_2)	4.953 ₈	16.364 ₂	3.303 ₄	2.47 ₇	3.06 ₈
T_{Co} (21% UCo_2)	4.953 ₁	16.362 ₂	3.303 ₄	2.47 ₇	3.06 ₈
T_{Co} (saturated with UCo_2)	4.952 ₉	16.361 ₄	3.303 ₄	2.47 ₇	3.06 ₈

* This structure is complicated and the distances given above are approximate, being for the ideal structure with axial ratio 3.267:

$$d_{M-M} = a/2; d_{U-U} = 3c/16$$

TABLE IV.—*Lattice Spacings and Interatomic Distances for Alloys with C15 Structure, After Quenching from 900° C.*

Composition	Lattice Spacing, (<i>a</i> ₀), kX	Interatomic Distance, kX *	
		<i>d_{M-M}</i>	<i>d_{U-U}</i>
UMn_2 (as cast)	7.142 ₈	2.525 ₃	3.092 ₈
UMn_2 (ref. 5)	7.148 ₄
UFe_2	7.051 ₀	2.492 ₉	3.053 ₁
UFe_2 (containing 50% UNi_2)	7.033 ₂	2.486 ₆	3.045 ₄
UFe_2 (saturated with UNi_2)	7.044 ₅	2.490 ₆	3.050 ₃
UFe_2 (saturated with UNi_2 at 1000° C.)	7.025	2.484	3.040
UFe_2 (ref. 5)	7.045 ₂
UFeNi (ref. 5)	7.040
UCo_2	6.991 ₀	2.471 ₇	3.027 ₁
UCo_2 (containing 65% UNi_2)	7.027 ₄	2.484 ₅	3.042 ₉
UCo_2 (ref. 5)	6.978 ₃

$$* d_{M-M} = \frac{a\sqrt{2}}{4}; d_{U-U} = \frac{a\sqrt{3}}{4}$$

this has been found. An alloy containing 17.4 at.-% iron, heat-treated at 1000° C., quenched and reheated at 700° C. for periods of up to 4 weeks before final quenching, yielded a series of parameter values increasing with time of annealing at 700° C. towards the values obtained by heat-treatment at 900° or

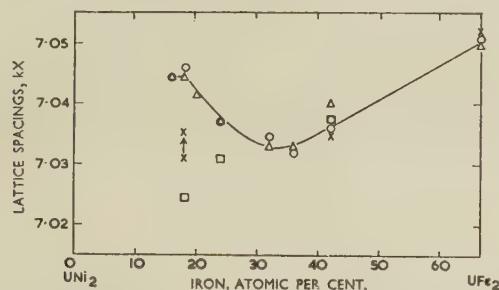


FIG. 9.—Showing Variation of Lattice Parameter with Composition of *C15* Structure in $\text{UNi}_2\text{--UF}_6_2$ Section.

KEY.

- Quenched from 700° C.
 △ " " 900° C.
 □ " " 1000° C.
 × " " 700° C., after slow cooling from 1000° C.

700° C. This was accompanied by precipitation of the phase believed to be based on *X* (U-Ni). However, this phase could not be observed in alloys heat-treated at 900° C. only.

IV.—DISCUSSION AND CONCLUSIONS

The ranges of composition of the Laves phases in the pseudo-binary sections showed two characteristic features:

(i) At 900° C. the range of the two terminal solid solutions, based respectively on the *C15* (e.g. UMn_2) and *C14* (UNi_2) structures, became rather more restricted on passing from manganese to iron to cobalt. At 700° C. the phase boundaries were only slightly different, except for an increased solubility of cobalt in UNi_2 .

(ii) The stability range of the intermediate phase with the *C36* structure was widened on passing from manganese to iron to cobalt.

1. SIZE-FACTOR CONSIDERATIONS

The type of structure assumed by a Laves phase depends mainly on the relative sizes of the atoms of the component metals.⁴ Table V compares the interatomic distances in the binary uranium Laves phases with those in the pure metals. The ratios d_U/d_M all lie fairly close to the ideal ratio of 1.225 and are consistent with the general observation of Berry and Raynor that the *C14* structure is formed at or near the ideal ratio, 1.225, and that as the ratio d_A/d_B in AB_2 is increased or decreased from this figure, it is replaced by the *C15* structure.

The contraction of the interatomic distances between the *M* atoms in the binary phases UM_2 , as compared with those in the metal in the pure state,

decreased progressively from manganese to nickel, whilst the contraction in uranium increased. The mean interatomic distance of nickel atoms in UNi_2 increased slightly. Hence the effective size of the nickel in these phases was greater than that of cobalt. The interatomic distance of iron atoms in UFe_2 was intermediate between the two nickel distances in UNi_2 .

The larger effective size of nickel was reflected in the increases of parameter in each structure as nickel replaced cobalt (Tables II, III, and IV). In the iron-containing *C14* and *C36* structures nickel behaved as

TABLE V.—Comparison of Interatomic Distances in Laves Phases with Those in the Pure Elements.

Element	Interatomic Distance, kX		Contraction, %	d_{U-U} (in UM_2)	Contraction, %	Ratio d_U/d_M (pure metals)
	d_M (pure metal)	d_{M-M} (in UM_2)				
Mn	2.59 *	2.525	2.32	3.093	0	1.193
Fe	2.54 †	2.493	1.97	3.053	1.29	1.217
Co	2.501 †	2.472	1.20	3.027	1.94	1.236
Ni	2.487 †	2.475	0.48	3.193	-3.24	1.241
		2.504	-0.71	3.003	2.91	
U	3.09 †

* Extrapolated from lattice parameters of γ -manganese in Table X of ref. 13.

† From Tables IX and XI of ref. 13.

if it were smaller than the iron atom. The parameter/composition curve for the *C15* structure (Fig. 9) shows that replacement of iron by nickel decreased the *M-M* distance until half the iron had been replaced. Beyond this point, there was an increase at 900° C. in *M-M* distance in the direction of the higher nickel interatomic distance.

The minimum parameter at the equiatomic iron : nickel ratio suggests the possibility of ordering of nickel and iron atoms, but whether this is so is impossible to determine by X-ray methods, owing to the similarity in scattering power of the two atoms.

Consideration of the relative sizes of the atoms can account qualitatively for the general trend in lattice parameter in each phase field of the ternary Laves phases, but it is difficult to relate this to the ranges of stability of each structure.

2. ELECTRONIC CONSIDERATIONS

In magnesium-based Laves phases, where the d_A/d_B ratio is close to the ideal, the *C14* structure (MgZn_2) is associated with high electron : atom ratios of about 2, and the *C15* (MgCu_2) with lower ratios of less than 1.76.

The d_U/d_M ratios in uranium-based Laves phases also lie close to the ideal value, so that the pseudo-binary sections might also be controlled by considerations of electron-valency number.

It is generally accepted that the transition metals appear to have valencies which vary with their environment. In alloys with a metal of high valency,

such as aluminium, their alloying behaviour may be accounted for by the apparent valency increasing from -3.66 for manganese to -0.6 for nickel;¹ in copper-base alloys with aluminium or zinc, manganese, iron, cobalt, and nickel behave as if they had valencies of 1.9 , 1.0 , 0.8 , and 0.6 , respectively.¹⁴ In alloys of the transition metals alone there is little evidence to indicate their apparent valencies.

By analogy with the magnesium alloys, the apparent valency of nickel in the uranium Laves phases must be greater than that of manganese, iron, or cobalt. On the assumption that the limit of solubility of the latter elements in UNi_2 corresponds to the same electron : atom ratio, then the apparent valencies decrease in the order manganese, iron, cobalt. On the other hand, by making a similar assumption about the solubility of nickel in UMn_2 , UFe_2 , and UCo_2 , the apparent valencies decrease in the order cobalt, iron, manganese. From Laves phases where A is gadolinium, titanium, zirconium, niobium, or tantalum, assumed to exert valencies of 3 , 4 , 4 , 5 , and 5 , respectively, and B is manganese, iron, cobalt, or nickel, Pfeil and Waldron¹⁵ have deduced that the latter elements have respective valencies of approximately 0.7 , 0.7 , 1.5 , and 2.0 . Assuming constant valency, they further deduce a valency of approximately 2 for uranium in its Laves phases. If their valencies are modified so that manganese has about 0.65 , iron 0.75 , and cobalt 0.85 , the limit of solubility of nickel in UMn_2 , UFe_2 , and UCo_2 occurs at an electron : atom ratio of 1.76 , conforming with the solubility limits of various elements in MgCu_2 .

The first prominent lines in the Debye-Scherrer pattern of the $C15$ structure are 220 and 113 , with a weaker 222 line. Witte, Klee, and Lieser¹⁶ found the Brillouin zone of this structure to be bounded by (113) and (222) planes, resembling a sphere and containing 1.8 electrons/atom. The inscribed Fermi sphere to (113) planes, however, corresponds to an electron : atom ratio of 1.59 , and there is the possibility of an overlap occurring on certain 113 faces. This would be reflected in an expansion of the lattice in $[113]$ directions, i.e. representing in a cubic lattice an increase in lattice parameter. In the UFe_2 solid solution, using the electron-valency values of 2 for uranium and nickel and 0.75 for iron, the minimum in the lattice parameter/composition curve (Fig. 9) would occur at an electron : atom ratio of 1.58 , suggesting that an explanation of this fact might involve electronic factors in addition to atomic size.

However, a more rigorous treatment is required to determine this point. Insufficient results are available for similar anomalies to be sought in the UMn_2 and UCo_2 phase fields. This simple approach is also inadequate to account for the ranges of stability of the other phase fields. The electron-valency numbers employed above do not lead to constant electron : atom ratios for any other phase boundary.

In conclusion, it seems unlikely that the equilibria in these three pseudo-binary sections can be accounted for by simple considerations of size-factor or electron : atom ratios, and a proper understanding must await further developments in alloy theory.

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REFERENCES

1. G. V. Raynor, "Progress in Metal Physics", Vol. I, p. 1. 1949: London (Butterworths Scientific Publications).
2. F. Laves and H. Witte, *Metallwirtschaft*, 1936, **15**, 840.
3. F. Laves and H. Witte, *ibid.*, 1935, **14**, 645.
4. K. H. Lieser and H. Witte, *Z. Metallkunde*, 1952, **43**, 396.
5. H. Witte, *Z. angew. Mineral.*, 1937, **1**, 83.
6. R. L. Berry and G. V. Raynor, *Acta Cryst.*, 1953, **6**, 178.
7. K. Kuo, *Acta Met.*, 1953, **1**, 720.
8. N. C. Baenziger, R. E. Rundle, A. I. Snow, and A. S. Wilson, *Acta Cryst.*, 1950, **3**, 34.
9. P. Gordon, *U.S. Atomic Energy Commission Publ.*, 1952, (AECU-1833).
10. H. A. Wilhelm and O. N. Carlson, *Trans. Amer. Soc. Metals*, 1950, **42**, 1311.
11. J. B. Nelson and D. P. Riley, *Proc. Phys. Soc.*, 1945, **57**, 160.
12. G. E. Bacon, *Acta Cryst.*, 1948, **1**, 337.
13. G. I. Williams and T. J. Heal, unpublished work.
14. J. D. Grogan and R. J. Pleasance, *J. Inst. Metals*, 1953-54, **82**, 141.
15. W. Hume-Rothery and G. V. Raynor, "The Structure of Metals and Alloys", 3rd edn., pp. 92-94. 1954: London (Inst. Metals Monograph and Report Series No. 1).
16. J. B. Haworth and W. Hume-Rothery, *Phil. Mag.*, 1952, [vii], **43**, 613.
17. P. C. L. Pfeil and M. B. Waldron, *Atomic Energy Research Estab. Rep.*, 1950, (M/R 581).
18. H. Witte, H. Klee, and K. H. Lieser, *Naturwiss.*, 1951, **38**, 185.

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SYNOPSIS

The uranium-zirconium system has been examined by metallographic, dilatometric, and X-ray methods, using alloys prepared by arc melting. A continuous series of body-centred cubic solid solutions is formed between γ -uranium and β -zirconium. At 14.5 at.-% zirconium the γ phase exists up to $693^\circ \pm 3^\circ \text{C.}$, where it undergoes a monotectoid reaction; at 69.5 at.-% zirconium it exists up to $606^\circ \pm 3^\circ \text{C.}$, where it transforms by a eutectoid reaction. A miscibility gap is formed at 693°C. from 14.5 to about 57 at.-% zirconium; this reaches a maximum at $740^\circ \pm 5^\circ \text{C.}$, and 34 at.-% zirconium.

The maximum solubility of zirconium in β -uranium is 2.5 at.-% at 693°C. ; the β solution transforms by a eutectoid reaction at $662^\circ \pm 2^\circ \text{C.}$, *ca.* 1.5 at.-% zirconium. The maximum solubility of zirconium in α -uranium at the eutectoid is placed tentatively at about 1 at.-%; the eutectoid transformation extends to approximately 61 at.-% zirconium. The solubility of uranium in α -zirconium is estimated to be 0.75 at.-% at 606°C.

It was not found possible to completely retain the γ solution by quenching either lumps or powders containing up to 35 at.-% zirconium. It was retained completely, however, in the 40 at.-% zirconium alloy. The β -uranium solution containing 2.5 at.-% zirconium could not be retained by quenching.

I.—INTRODUCTION

URANIUM crystallizes in three allotropic modifications. The α form has an orthorhombic structure¹ and exists from room temperature up to $665^\circ \pm 3^\circ \text{C.}$ ² The β form is stable from 665° to $772^\circ \pm 3^\circ \text{C.}$, and Tucker³ has shown that it has a complex tetragonal structure. The γ modification, which exists from 772°C. to the melting point, has a body-centred cubic structure. Recent determinations have placed the melting point at 1133°C. ⁴ and $1090^\circ \pm 2^\circ \text{C.}$ ⁵; a purity of 99.96 wt.-% is given for the material in the latter case. Zirconium has two allotropic modifications: α , the low-temperature form, has a hexagonal close-packed structure, while β has a body-centred cubic structure. The transformation temperature has been reported as $863^\circ \pm 3^\circ \text{C.}$ ⁶, and values of $1830^\circ \pm 40^\circ \text{C.}$ ⁶ and $1845^\circ \pm 25^\circ \text{C.}$ ⁷ have been given for the melting point.

Little information has been published on uranium-zirconium alloys. According to Carlson,⁸ γ -uranium and β -zirconium form a continuous series of solid solutions at high temperatures. A eutectoid was found at 688°C. , 10 at.-% zirconium, and a further eutectoid was thought to occur at a lower temperature.

II.—EXPERIMENTAL METHODS

1. PREPARATION OF THE ALLOYS

The uranium used for the alloys was supplied by the Atomic Energy Research Establishment, Harwell, and its purity is considered to be higher than 99.95 wt.-%. Zirconium, prepared by the van Arkel

method, was obtained from the Philips Co., Eindhoven, Holland, and the Metropolitan-Vickers Electrical Co., Ltd. No information is available about the purity of this material, in particular its probable hafnium content, though this may well be of the order of 3 wt.-%. It is not considered likely, however, that the presence of hafnium will have any serious effect on the general shape of the equilibrium diagram, because of the close similarity of the two metals.

All alloys were prepared in an arc furnace under purified argon. Segregation was removed by annealing the specimens in the arc furnace, reducing the power until the alloy solidified, and maintaining these conditions for 30 min., turning the bead over after 15 min.

The alloys were further homogenized by annealing for 3 weeks at 1000°C. in evacuated silica tubes; contact between the alloys and the silica was prevented by means of alumina spacers.

2. ANNEALING TECHNIQUES

All subsequent heat-treatments were carried out in evacuated silica capsules, or in an atmosphere of purified argon, as described later. For lower-temperature anneals the specimens were wrapped in molybdenum foil and sealed in silica capsules after degassing at 400°C. and evacuating to 10^{-5} mm. Quenching was effected by withdrawing the capsule from the furnace and breaking it under water. No reaction was found between the alloys and the molybdenum up to 800°C. ; at temperatures above this, the alloys were separated from the silica by alumina. Annealing

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was carried out in tubular furnaces controlled to $\pm 1^\circ \text{C.}$ by platinum-resistance thermometer controllers.

3. DILATOMETRIC INVESTIGATION

The solid-state transformations in the alloys were investigated by dilatometry. A dilatometer made entirely from silica and based on a design by Bangham and Franklin⁹ was constructed for this purpose. Specimens for investigation, in the form of rods about 30 mm. long \times 5 mm. dia., were prepared by casting the alloys in a groove in the copper hearth of the arc furnace. These rods were then homogenized by annealing for 4 weeks at 1000°C. and, when the ends had been ground to the gauge-length, were ready for investigation. In the dilatometer the specimen was separated from the silica by spacers of fused alumina and the whole was evacuated to 10^{-5} mm. Heating rates of 1°C./min. were used, and the temperature was measured by means of a platinum/platinum-13% rhodium thermocouple placed in contact with the specimen.

4. METALLOGRAPHIC EXAMINATION

(a) Specimen Preparation

After the normal procedure of grinding on successively finer emery paper, the alloys were polished either with an aqueous suspension of magnesia on blanket felt or a suspension of diamond dust ($0\text{--}2\ \mu$) in white spirit on Selvyt cloth. Electrolytic polishing was employed for some of the uranium- and zirconium-rich alloys; for the former the bath contained ethyl alcohol 40, ethylene glycol 30, and phosphoric acid 30%, and for the latter 20% hydrofluoric acid in ethyl alcohol.

(b) Etching Techniques

On quenching, both the γ - and β -uranium phases decompose to give α . For uranium-rich alloys an etching reagent containing 50% nitric acid and 50% acetic acid was used for periods up to 10 min.; this differentiates between decomposed γ and decomposed β , the latter being attacked more rapidly than the former. At intermediate compositions, an aqueous solution of 10% potassium hydroxide and 10% potassium ferrocyanide was used, particularly for alloys consisting of a mixture of decomposed and retained γ ; the former is rapidly attacked by this reagent. To differentiate between α - and β -zirconium, a solution of 1% hydrofluoric acid and 5% nitric acid in water was used, which attacks α in preference to β .

5. HIGH-TEMPERATURE X-RAY PHOTOGRAPHY

A Unicam 19-cm. high-temperature X-ray powder camera, modified along the lines suggested by Berry, Henry, and Raynor,¹⁰ was used. Filings of the specimens were sealed in silica tubes of about $20\ \mu$ wall thickness, after evacuating and degassing at 400°C. A temperature calibration for this camera was ob-

tained from lattice-parameter measurements of gold, using the known coefficient of thermal expansion of the metal. To confirm the calibration, a succession of photographs of a specimen of pure uranium was taken at small temperature intervals until the structure, as shown by the diffraction pattern, had changed from α to β . The bracketing temperatures were found to be 664° and 668°C. , which agree well with the value of 665°C. which has been given for the transformation temperature.² It is considered that the specimen temperatures estimated in this way were correct to $\pm 5^\circ \text{C.}$ A Raymax 5-in.-dia. rotating-anode X-ray set was used, which gave satisfactory exposures in only 3 hr. This allowed short anneals to be given in the camera before exposure, and also permitted repeated exposures to be made at different temperatures, before the specimen became contaminated by reaction with the silica.

6. COMPOSITION OF THE ALLOYS

All the alloys were analysed for both uranium and zirconium by the Atomic Energy Research Establishment or the Chemical Inspectorate of the Ministry of Supply. In the majority of cases the analytical totals lay slightly below 100%, and there was a slight pick-up of aluminium and silicon, estimated spectroscopically to be of the order of 0.2%. No analysis was made of the hafnium content of the zirconium used in the preparation of the alloys.

III.—THE CONSTITUTIONAL DIAGRAM

The suggested form of the constitutional diagram is given in Fig. 1. The positions of the various phase boundaries are based on the metallographic and X-ray analyses of annealed and quenched specimens and on the dilatometric results. There are four solid phases: α , the α -uranium solid solution; β , the β -uranium solid solution; γ , the series of solid solutions formed between γ -uranium and β -zirconium; and δ , the α -zirconium solid solution. Where possible the phases present have been confirmed by high-temperature X-ray photography. The experimental evidence relating to the different phase fields is discussed below in detail.

1. THE MELTING POINTS

The liquidus was determined by measuring with an optical pyrometer the temperature of the liquid at the junction of a small pool of liquid maintained on the surface of the alloy bead in the arc furnace. These temperatures were corrected for adsorption and non-black-body conditions by an empirical curve derived from the known melting points of the secondary standards given in the International Temperature Scale of 1948.¹¹ Individual measurements of the melting points of these pure metals and of the alloys were reproducible to $\pm 10^\circ \text{C.}$ Liquidus values were obtained

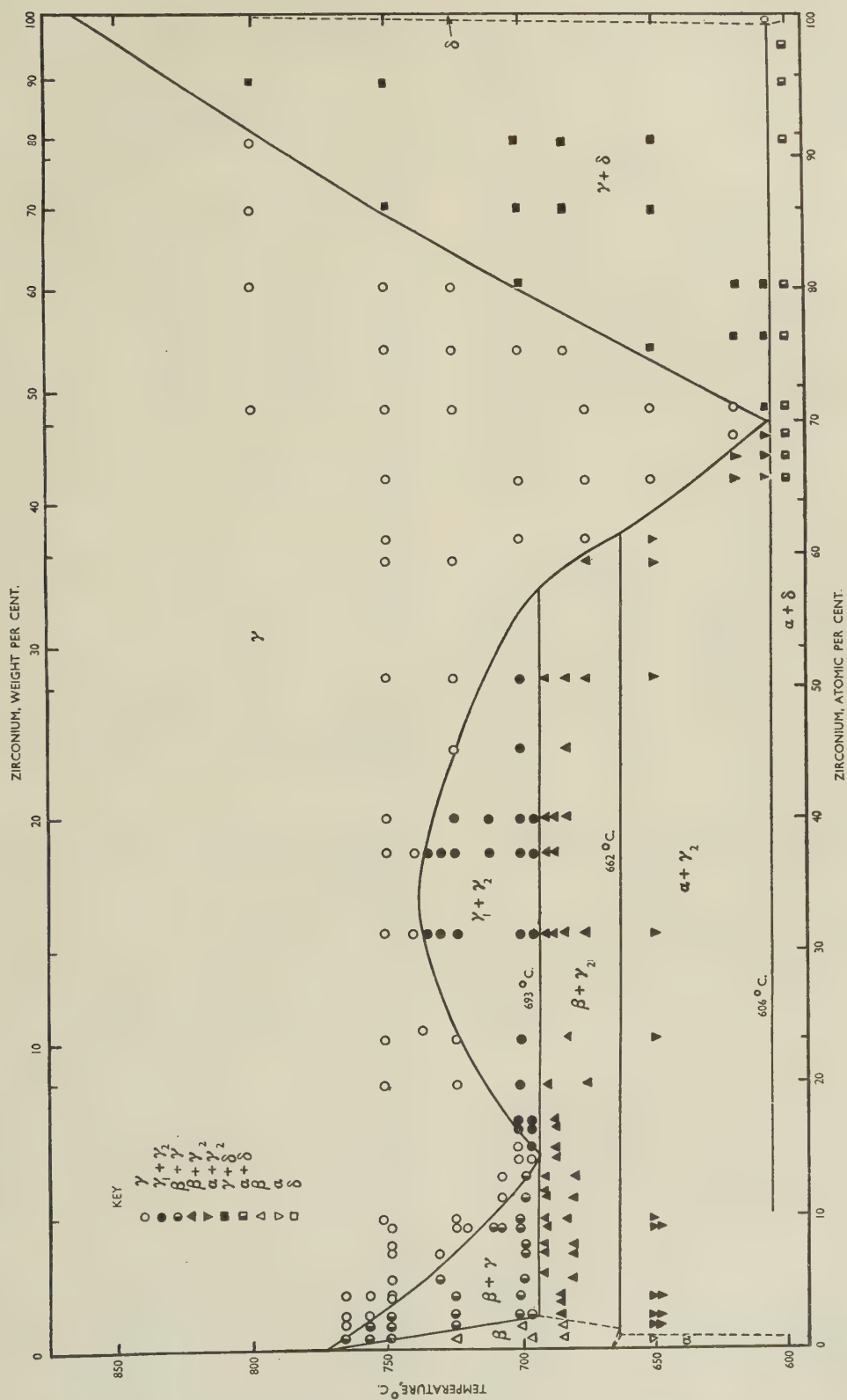


Fig. 1.—The Uranium-Zirconium System.

in this way for alloys containing from 40 to 100 at.-% zirconium; in the uranium-rich alloys, it was not possible to maintain a pool of liquid metal on the surface of the solid alloy owing to the formation of a skin, and no values could be obtained. The results are given in Table I, which shows both measured and calculated values.

The solidus temperatures for the 10, 30, and 50 at.-% zirconium alloys were bracketed by heating and quenching samples from successively higher temperatures until some chilled liquid was detected in the microstructure. The alloys were suspended in a small recrystallized alumina crucible inside a refractory tube, up which was passed a gentle stream of purified argon. After holding at temperature for 30 min., the specimen was quenched, by fusing the suspension wire, into a bath of low-vapour-pressure oil, cooled almost to its freezing point. The temperature of the specimen was measured by a thermocouple, the junction of

TABLE I.—*Melting Points of Uranium-Zirconium Alloys.*

Zirconium at.-%	Solidus Temp., °C.		Liquidus Temp., °C.	
	Lower Bracket	Upper Bracket	Measured	Calculated
10	1160	1200
30	1250	1300
40	1420	1510
50	1400	1450	1460	1560
60	1530	1640
70	1600	1725
80	1670	1810
100	1700	1840

which was located inside the crucible. The results of the solidus determinations are included in Table I.

2. THE γ SOLID SOLUTION

A series of alloys at composition intervals of 5 at.-% were examined metallographically after quenching from 1000° C. and again after subsequent anneals at 900°, 800°, and 700° C. for 7 days. At 1000° C. the alloys showed equiaxed grain structures from 40 to 90% zirconium; the remaining uranium-rich alloys and the 95 at.-% zirconium alloy had acicular decomposition structures. X-ray powder photographs confirmed the existence of a body-centred cubic structure from 40 to 90 at.-% zirconium. The parameters of this phase varied linearly with composition, extrapolating to 3.51 kX at 100% uranium and 3.58 kX at 100% zirconium. The latter value agrees with that given by Duwez¹² for β -zirconium at room temperature. The former is somewhat higher than the value given for γ -uranium; this is, however, not surprising in view of the long extrapolation.

At 700° C. single-phase alloys were found only at 15 and 20 at.-% zirconium and between 55 and 75 at.-% zirconium. These results suggest that γ -uranium and β -zirconium form a continuous series of solid solutions.

3. THE SOLID-STATE TRANSFORMATIONS

The results of a dilatometric examination of a range of alloys are given in Table II. The temperatures are

TABLE II.—*Temperature of Dilatometric Transformations.*

Zirconium at.-%	Transformation 1		Transformation 2		Transformation 3	
	Heating	Cooling	Heating	Cooling	Heating	Cooling
	°C.	°C.	°C.	°C.	°C.	°C.
2.5	677	645
5	699	689	676	638	614	602
7.5	703	692	675	647	613	597
10	697	690	668	647	606	601
12.5	693	680	673	658	610	602
15	...	675	667	...	606	606
20	692	671	669	662	611	601
30	687	668	664	...	607	605
50	691	665	664	...	610	607
65	612	609
66.7	611	608
68	611	610
70	609	605
72.5	605	600
75	607	603
80	606	605
90	606	601
92	601	597
98	600	595

the means of four heating and cooling experiments; the results of successive measurements were reproducible to $\pm 3^\circ$ C. Three transformations were detected, at approximately 690°, 660°, and 600° C., with maxima at 15, 2.5, and 70 at.-% zirconium, respectively.

It is considered that the transformation at 690° C. is a monotectoid one. A series of alloys annealed for 14 days and quenched from 700° C. were two-phase between 2.5 and 11.3 at.-% zirconium, single-phase at 14.1 and 15.1 at.-%, and two-phase from 16.6 to 50.2 at.-% zirconium. After annealing at 691° C. a two-phase structure was obtained over the entire composition range from 5.6 to 50.2 at.-% zirconium.

In an X-ray photograph of a 5.6 at.-% zirconium alloy taken at 721° C. both β - and γ -uranium patterns were identified. The limits of the ($\beta + \gamma$) region were determined by annealing selected alloys at temperatures from 696° to 765° C. The results of the metallographic examination of these alloys are indicated in Fig. 1. A typical microstructure from the ($\beta + \gamma$) region is illustrated in Fig. 2 (Plate XL), which is of a 4 at.-% zirconium alloy annealed at 724° C.

The series of alloys containing 15.1–60.8 at.-% zirconium, quenched from 700° C., showed a continuous transition from one solid-solution structure to another. The uranium-rich phase in these alloys had decomposed on quenching, the other phase being retained. At higher temperatures the two-phase region decreased in extent, as shown by the metallographic results included in Fig. 1. A typical microstructure for the miscibility-gap region is illustrated in

Fig. 3 (Plate XL). This shows a 37.2 at.-% zirconium alloy annealed at 712° C.: the γ_1 solution has decomposed to α , and has etched dark, while the γ_2 solution has been retained.

It was not possible to obtain an X-ray photograph showing both body-centred cubic patterns in the $\gamma_1 + \gamma_2$ region. A 31.1 at.-% zirconium alloy was photographed at 702° C. and then annealed in the camera for 24 hr. and re-photographed. One body-centred cubic pattern was clearly defined and in addition some diffuse lines were visible; these, however, could not with certainty be identified as belonging to a second body-centred cubic pattern. In a further attempt to obtain a photograph from this region, a specimen of a 37.2 at.-% zirconium alloy was annealed for 7 days at 709° C. and water-quenched; filings were then heated in the camera to 709° C. This required about 20 min., and photographs were then taken after annealing for 1 hr. and 24 hr. in the camera. The results were similar to those on the 31.1 at.-% zirconium alloy. This specimen was then cooled to 675° C. and photographed; the β and γ_2 patterns were identified.

A number of alloys were annealed at temperatures from 680° to 700° C., to confirm the temperature of the monotectoid reaction. A 14.2 at.-% zirconium alloy annealed at 696° C. for 8 days was still single-phase γ ; whereas a 12.9 at.-% alloy at 698° C. consisted of ($\beta + \gamma$), and a 17.1 at.-% zirconium alloy at 696° C. of ($\gamma_1 + \gamma_2$). A series of alloys from 5.6 to 50.2 at.-% zirconium annealed at 691° C. were all $\beta + \gamma$. On the basis of this metallographic and dilatometric evidence the monotectoid is placed at 14.5 ± 0.5 at.-% zirconium and $693^\circ \pm 3^\circ$ C.

The second transformation is considered to be due to the decomposition of the β -uranium solid solution. X-ray powder photographs of a 31.3 at.-% zirconium alloy revealed ($\beta + \gamma$) patterns at 663° and 690° C., but ($\alpha + \gamma$) patterns at 641° C. Some hysteresis was found in this transformation, increasing with uranium content; however, from a consideration of the dilatometric results on the alloys containing 20–50 at.-% zirconium the transformation temperature is placed at $662^\circ \pm 2^\circ$ C. It is assumed to be a eutectoid reaction, as the $\alpha \rightarrow \beta$ transformation occurs at 665° C.

The third transformation is due to the eutectoid transformation of the γ -uranium solid solution. A series of alloys in the range 65–75 at.-% zirconium were annealed at 619°, 608°, and 599° C. to determine the eutectoid composition. An X-ray examination of the alloys at 599° C. revealed both α -uranium and α -zirconium. At 608° C. γ was present in all of the alloys, and at 619° C. the 68.5 and 70.5 at.-% zirconium alloys were single-phase γ . On the basis of these results the eutectoid is placed at $606^\circ \pm 3^\circ$ C. and 69.5 ± 0.5 at.-% zirconium.

Compositions limiting the ($\beta + \gamma$) and ($\alpha + \gamma$) phase fields are shown in Fig. 1. The microstructure of a 50.3 at.-% zirconium alloy annealed for 21 days at 675° C. is illustrated in Fig. 4 (Plate XL). This shows β precipitated through the γ grains and along

the grain boundaries. In the 58.9 at.-% zirconium alloy after the same treatment β was present only at the grain boundaries and the 60.8 at.-% alloy was single-phase; α was precipitated directly from γ in the 50.3 at.-% alloy at 650° C., (Fig. 5, Plate XL). At 650° C. the 60.8 at.-% zirconium alloy was now two-phase, although that containing 65.2 at.-% zirconium was still single-phase γ .

4. THE SOLUBILITY OF ZIRCONIUM IN α - AND β -URANIUM

The solubility of zirconium in β -uranium was determined metallographically. Uranium-rich alloys containing up to 5 at.-% zirconium were annealed for 2 days at 800° C., and then transferred to furnaces at 765°, 756°, 748°, 724°, 700°, or 650° C. The preliminary annealing treatment at 800° C. was found to be sufficient to transform these alloys into homogeneous single-phase γ . Subsequent annealing times varied from 4 days at 765° C. to 30 days at 650° C. Further anneals of 21 and 30 days at 684° and 650° C. revealed no change in the microstructures. The results of the metallographic examination are included in Fig. 1. The solubility of zirconium in β -uranium is placed at 2.5 ± 0.5 at.-% at the monotectoid temperature. No metallographic determination of the β -eutectoid composition was possible owing to the difficulty of interpreting the microstructure of the uranium-rich alloys at this temperature. These were very finely divided, even after the extended annealing periods. From the dilatometric results, the eutectic is tentatively placed at 1.5 at.-% zirconium.

Owing to the fine nature of the microstructures, the limits of the α -uranium solid solution could not be determined with certainty. At 680° C. a 1.8 at.-% zirconium alloy appeared to be single-phase when examined after annealing for 4 weeks and again after 10 weeks; a 2.5 at.-% zirconium alloy after the same treatment was considered to be two-phase; similarly, a 1.8 at.-% zirconium alloy, annealed for 2 months at 600° C., was also considered to be two-phase. It seems probable that the maximum solubility of zirconium in α -uranium is less than 1 at.-%.

5. THE SOLUBILITY OF URANIUM IN α -ZIRCONIUM

The solubility of uranium in α -zirconium at the eutectoid temperature of 606° C. was determined by metallography and autoradiography. Samples of alloys containing 2.1, 1.3, 0.9, and 0.4 at.-% uranium were cold rolled to 50% reduction, annealed for 48 hr. at 606° C., and water-quenched. The cold-working and heat-treatment cycle was repeated and the alloys examined metallographically after electropolishing in 30% hydrochloric acid in alcohol. The 0.4 at.-% uranium alloy was single-phase, the remainder two-phase.

A uranium rod was forced into a hole in a sample of zirconium and the specimen annealed for 2 months at 606° C. Autoradiographs were taken of a section through the specimen, and of two alloys containing

2.1 and 5.0 at.-% uranium quenched from the γ region, using nuclear emulsion plates. Very little diffusion of uranium into the zirconium had taken place, and thus there existed only a very narrow region of the equilibrium α -zirconium solid solution; consequently, it was not possible to make accurate track counts for the solid-solution region. A comparison with the two standard alloys, however, enabled the solubility to be estimated as 1.0 ± 0.5 at.-% uranium.

As a result of these experiments the maximum solubility of uranium in α -zirconium is considered to be between 0.4 and 1.0 at.-% at 606° C.

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REFERENCES

1. C. W. Jacob and B. E. Warren, *J. Amer. Chem. Soc.*, 1937, **59**, 2588.
2. P. Duwez, *U.S. Atomic Energy Commission Publ.*, 1952, (AECD-3421; NAA-SR-169).
3. C. W. Tucker, Jr., *Trans. Amer. Soc. Metals*, 1950, **42**, 762; *Acta. Cryst.*, 1951, **4**, 425.
4. A. I. Dahl and H. E. Cleaves, *J. Research Nat. Bur. Stand.*, 1949, **43**, 513.
5. A. Allendörfer, *Z. Naturforsch.*, 1950, [A], **5**, 234.
6. F. W. Boulger, *U.S. Atomic Energy Commission Publ.*, 1949, (AECD-2726).
7. D. J. McPherson, quoted by H. K. Adenstedt, *Trans. Amer. Soc. Metals*, 1952, **44**, 949.
8. O. N. Carlson, *U.S. Atomic Energy Commission Publ.*, 1951, (AECD-3206; ISC-102).
9. D. H. Bangham and R. E. Franklin, *Trans. Faraday Soc.*, 1946, **42B**, 289.
10. R. L. Berry, W. G. Henry, and G. V. Raynor, *J. Inst. Metals*, 1950-51, **78**, 643.
11. — "The International Temperature Scale, 1948". 1950: London (H.M. Stationery Office).
12. P. Duwez, *J. Inst. Metals*, 1951-52, **80**, 525.

THE CHOICE AND CONSTRUCTION OF MONOLITHIC LININGS FOR TWIN-BATH INDUCTION FURNACES FOR MELTING ALUMINIUM ALLOYS*

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SYNOPSIS

Considerable difficulties have been met with in establishing a satisfactory practice for the formation of a lining possessing the necessary metallurgical, mechanical, and thermal properties to withstand the severe service conditions sometimes encountered in a large, twin-bath, low-frequency induction furnace employed for melting aluminium alloys. Several techniques and various types of lining, the possibilities of which have been explored, are briefly described, and reasons are set out for the final choice of a densely rammed, fully monolithic lining, formed and fired *in situ*.

Sections are also included on the design of steel lining formers, extraction tools, and other accessories; preparation of the refractory mix; ramming procedure; the firing of the lining; and the ultimate commissioning of the furnace.

I.—INTRODUCTION

ELECTRICAL energy as a heating agent, with its inherent flexibility and accuracy of temperature control, commends itself to the metal industry as an aid in meeting the increasingly stringent specifications laid down by the consumer. The induction melting furnace has certain specific advantages over other types, which may be briefly summarized as follows:

(i) The elimination of a gaseous atmosphere, the temperature of which is well in excess of that of the metal, leads to improvements in the metal quality in respect of gaseous and solid impurities.

(ii) The reduction in melt loss due to oxidation and volatilization is particularly significant where light-gauge scrap is to be melted; with this type of material a high loss is to be expected in the reverberatory-type furnace.

(iii) Improved alloying conditions and homogeneity of the melt result from the natural stirring action characteristic of the electro-dynamic forces within the molten metal.

(iv) Since the heat is generated within the body of the metal by its resistance to the flow of the induced current, the temperature, even in the melting channels, does not greatly exceed the final operating temperature of the melt.

These advantages make for high efficiency, and to some extent off-set other adverse economic factors. The balance is naturally somewhat influenced by the duty required of the furnace and the type of material charged.

Induction furnaces, both of the submerged-channel and the coreless type, have been used for the melting of brass, copper, and steel for many years, but although the melting of aluminium by this method is by

no means a recent innovation, it has not advanced to the same degree. Its application has been considerably retarded by the problem of constructing a refractory lining possessing suitable metallurgical and mechanical properties to give economic durability.

Linings naturally vary in intricacy. Those of the coreless-type induction furnace, being of a plain crucible shape, are simple in constructional detail. The single-bath, vertical-channel furnace is generally considered in two parts, i.e. the charging bath, which is not difficult to line, and the induction-unit casing, which, although fairly complicated, can in most cases be lined separately. The twin-bath, horizontal-channel type of furnace presents the most exacting problem, owing to intricacy of shape and the necessity for installing the whole lining, comprising the baths and the melting channels, in one operation.

The present paper reviews in some detail the factors leading up to the choice of a dense monolithic refractory lining for a twin-bath, horizontal-channel, low-frequency induction furnace used for melting aluminium alloys; the methods employed in its formation, and its characteristics in operation are also described. No attempt is made to deal with the relative merits of other types of furnaces and their linings, or of linings intended for the melting of metals other than aluminium. It is assumed that the fundamental problems associated with the lining of aluminium-melting furnaces are appreciated.

II.—PRODUCTION AND MAINTENANCE CONDITIONS AFFECTING LINING LIFE

The governing factors in the choice of material and method of formation of induction-furnace linings are:

(1) Compliance with metallurgical requirements.

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(2) Durability under conditions of thermal stress and shock, mechanical wear and tear due to charging and maintenance, and erosion due to flow of molten metal.

(3) Ease of manipulation of the material during installation of the lining or for repair work.

(4) Economic level of material cost.

The conditions under which such furnaces may operate vary between two extremes. On the one hand, a furnace feeding, say, a die-casting unit, where temperature control is an extremely important consideration, may be called upon to provide relatively small weights of metal for each cast, with correspondingly small charges of cold metal. As the bath is worked with the maximum content, the melt level and temperature are maintained within narrow limits, and from most points of view the furnace will be operating under the optimum thermal conditions as far as the lining is concerned. At the other extreme, representing severe operating conditions for a lining, is the large-capacity furnace used for bulk scrap melting, where the offtake weight represents the greater portion of the total capacity, the molten-heel weight being only that necessary effectively to seal the melting channels at maximum power tap. The linings which form the subject of this paper can be classified under the latter service conditions, the principal details being as follows:

Twin-bath furnaces with four horizontal melting channels:			
Channel cross-section approx.	.	.	$4\frac{3}{4} \times 4\frac{3}{4}$ in.
Furnace rating	.	.	450 kW.
Molten-heel capacity	.	.	1.5 tons
Offtake capacity	.	.	3.75 tons
Control temperature	.	.	720°–740° C.

A sketch of the furnace, showing the outline of the lining and approximate dimensions is given in Fig. 1.

Experience has shown that bulk charging into the molten heel is the most economical method as regards handling and power costs. In order to economize in power consumption, the bath is operated at the minimum possible temperature during melting, and by making the initial charge as large as possible consistent with the space available below the bath lid, the metal temperature falls rapidly to about 650° C. minimum with full power on. When melting scrap, it is necessary to make several bulk charges during each melt, the successive charges being supplied when space permits, or as soon as the temperature begins to rise. When the full weight has been charged, the temperature is allowed to rise to the required control figure, and the melt is taken off as soon as possible after this.

By this system minimum heat losses are incurred, and some degree of preheating of the charged metal in the space above the molten metal is achieved. Thermal equilibrium, however, is not normally reached in the lining before removing the metal and beginning the cycle again; consequently fairly severe conditions are imposed both in the melting bath and in the channels. For example, in the bath the temperature varies from, say, 730° C. at the end of the melt, to the chilled temperature imposed by the next bulk charge,

which may be made only 8 min. later. As a result, a fairly severe temperature gradient is set up vertically in the bath walls, accompanied by temperature variations through the thickness of the walls. In the channels the thickness of the lining is a minimum adjacent to the cooling-air tunnels surrounding the transformer coils; the temperature of the metal is a maximum at this point, and severe temperature gradients are set up. These gradients are altered each time the furnace is recharged and the metal temperature lowered. Moreover, since a temperature variation exists between

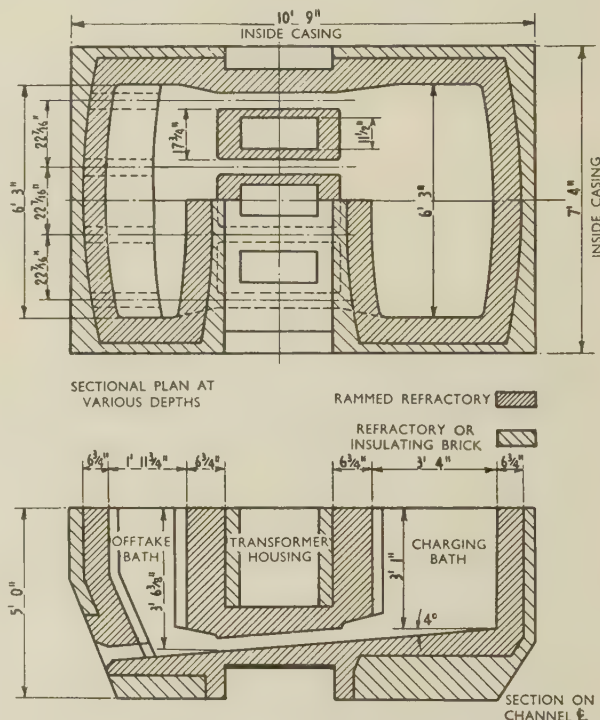


Fig. 1.—Outline of Lining and Approximate Dimensions. (Not to scale.)

the baths and the channels, temperature stresses are induced at the junction of the channel block and the bath walls.

In order to obtain access for cleaning the channels, it is necessary to remove the sealing plugs from the ports in the back wall, and this in turn necessitates switching off the power and back-tilting the furnace about 30° to bring the ports above the level of the molten heel, then almost completely contained in the charging bath. This results in the cooling of the offtake bath and the exposed sections of the melting channels. The cleaning operation occupies about 45 min.; meanwhile the charging bath, about one-third full of molten metal, is maintained at about 700° C., but with slow cooling of the exposed upper wall surfaces. Thus, the cleaning operation imposes yet another set of thermal stresses on the lining.

Further adverse thermal conditions may result from the failure of the power supply to the transformer unit for one reason or another. In such circumstances, it

is usual to try to reduce the contents of the furnace to the normal "heel" capacity, and to supply sufficient heat by means of gas burners inserted into the two baths to offset the heat losses and to keep the metal molten by flame impingement on the surface. This produces a complete reversal of the normal thermal conditions, since the channels, &c., will cool, while the exposed bath walls become heated by the gas flame.

From these examples it will be clear that the refractory lining employed in this type of furnace must be capable of withstanding quite severe thermal shock and stress. In addition, the lining has also to resist mechanical stresses, which may be due to a variety of causes, such as the following:

Bulk charging is carried out by tipping from bins which may contain up to 4000 lb. of scrap. Light scrap, such as swarf or cut-edge trimmings, is unlikely to cause trouble, but impact shock must result from charging plate, coil scrap, &c., and these materials will damage the charging-bath walls and floor, and inflict numerous chipping blows.

When charging pig by hand, the usual practice is to protect the bath floor with a "mattress" of sheet or similar scrap, and care is taken to stack the pig fairly evenly; nevertheless, pigs become displaced and occasional blows to the lining result.

As mentioned previously, it is necessary to clean out the channels at regular intervals. This is accomplished by forcing a broaching tool up the channels. Three tools are used, each having a blade which progressively opens out the channel profile from $\frac{1}{4}$ in. undersize, via $\frac{1}{8}$ in. undersize, to the full operating size. If, as a result of melting dirty scrap, it is necessary to hammer the tools through, severe mechanical shocks are inevitably imposed on the lining, which is relatively thin in this vicinity. Cleaning is vitally important to prevent serious reduction in the channel cross-section, which would jeopardize the melting efficiency and the ultimate life of the lining, and is carried out on a routine basis at least twice in a working week.

Obviously, for metallurgical reasons, it is desirable to maintain the bath walls in as clean a condition as possible, and it is therefore necessary to remove the slag and oxide encrustations regularly. This is usually done as the melt is taken off, when the deposits are fairly plastic, but some force has to be applied to the scraping tools to detach the more stubbornly adherent patches, and this causes additional stress to the lining.

The lining of the furnace is also subjected to continuous vibration when the induction unit is on full power; this can, of course, be minimized by careful assembly of the transformer, but it is detectable over the whole furnace, and is particularly apparent in the vicinity of the transformer housing. This vibration manifests itself in a gradual powdering of the lining at its interface with the shell brickwork insulation, but this does not prove serious unless the lining is poor in quality and of a crumbling nature.

Other mechanical stresses of a local nature some-

times arise from the need to "bar over" unmelted pig or heavy scrap in the bath, or to break down "bridges" which may occur in a charge of light scrap just above the molten metal level.

Finally, very severe mechanical stresses are imposed on the lining if a flash-over occurs in the transformer owing to an electrical fault. This produces the effect of a minor explosion, but a mechanically strong lining has proved capable of withstanding such shocks.

The foregoing examples indicate the nature of the stresses which any lining must be called upon to resist in normal service and under the emergency conditions which may develop from time to time.

III.—REFRACTORY MATERIALS AND METHODS OF LINING FORMATION

The metallurgical, thermal, and mechanical conditions which prevail during the melting of aluminium in a furnace of the type under consideration, demand the following properties in the lining:

(1) It should be of a glazed or "fritted" nature, so as to afford characteristics as nearly "non-wetting" as possible.

(2) The surface and the body of the lining should be as nearly as possible impermeable to the melt.

(3) The material behind the lining surface should remain "un-burnt" and retain the maximum degree of strength and resilience, in order to absorb the thermally and mechanically imposed stresses.

(4) Consistent with (1), (2), and (3), the complete lining should have as high a resistance to heat flow as possible, in order to keep power consumption to a minimum.

1. CAST LININGS

An early type of lining installed in the twin-bath furnace, consisted of a proprietary brand of refractory cement; this was used to form the bath floors, the melting-channel block, and a monolithic envelope behind refractory-brick bath walls. The castable refractory cement was an obvious choice as being simple and rapid in application. Cast linings had also been successfully used in smaller channel-type melters.

Certain difficulties were, however, experienced during the forming of the cast lining in avoiding cavities and spongy areas, since the shape of the furnace and the lining-former assembly resulted in "blind" spots and severely restricted access for "punning" or floating down the refractory. A further difficulty was that the extensive surface areas exposed during casting were prone to lose moisture in excess of that allowed for in the initial mix, making for hazardous bonding between any layers where, for constructional reasons, operations had to be temporarily discontinued.

This lining failed almost immediately after starting up, owing to penetration of molten metal into the channel block through cavities and cracks which opened

up in the lining. On breaking out, some sections of the lining were found to be almost granular in consistency. Doubtless, it would have been possible to make the use of a cast lining a more workable proposition by redesign of certain features in the vicinity of the transformer housing; however, basic design difficulties in improving means of access became apparent and experiments with this type of lining were not continued.

2. REFRACTORY-BLOCK LININGS

Some consideration was then given to linings formed from tongued and grooved, specially shaped, pre-fired refractory blocks, but apprehension was felt regarding the security of the joints. It was necessary to depend upon the skill of the bricklayer to produce uniformly thin joints throughout; moreover, the drying-out temperature would react differently upon the jointing cement and the refractory blocks and create an additional hazard that the surface joints might become potential lining cracks. In view of these drawbacks, and of the expense of the specially shaped refractory blocks, it was felt desirable to avoid surface lining joints altogether, and it was finally decided to form a fully monolithic rammed lining which would be fired *in situ*.

3. RAMMED LININGS

So far, three ramming methods have been tried; these are described below in the detail which their success in service seems to warrant.

The refractory materials used for all the rammed linings were of the acid type, being based on approximately 72% silica clay and 28% quartz. For the flat-rammed lining, however, about 10% additional silica was used with 4% silicate of soda, in a finer mixture. In all cases the moisture content was maintained between 5.2 and 6.5%.

Experience has shown that for successful "fritting" of the hot face, the composition of the lining must be such as to require a low "fritting" temperature, the reactivity of the silicic acid in the clay base being essential to promote "fritting", which may be described as a reaction between the acid and the oxide in the molten charge.

(a) Flat Ramming

This type of lining was in practice tried out in a single-bath type, vertical-channel furnace operating under similar conditions. The experience gained, however, served to illustrate the possibilities of such a lining.

The linings were formed by pneumatic hammers delivering approximately 1400 blows/min. at 80–90 lb./in.²; the compacting tools had flat working faces with a contact surface of $3 \times 1\frac{1}{2}$ in.

The lining material was spread in layers of approximately $2\frac{1}{2}$ in. loose depth, and then solidly compacted to about $1\frac{1}{2}$ in., using as many hammers as could gain access. Each layer was completed by a rapid pass of

the hammer with the tool angled to give a serrated finish about $\frac{1}{4}$ in. deep. The surface of the layer was then chipped crosswise with hand-tools, and all material dislodged was carefully removed. The object of this was to form a lock-bond to knit each successive compacted layer to the next. The formers were of mild steel, and were lightly oiled to prevent adhesion of the lining material.

Work was carried out continuously and was completed in 10 hr., inclusive of assembly and removal of formers. The weight of lining material rammed was approximately 7000 lb.

This method of application produced linings of a dark-brown, close-grained appearance, having a generally polished surface, but the boundaries between the layers were clearly defined by horizontal bands of less tightly packed refractory, resulting from the disturbance of precompact material when chipping the surface of each compacted layer.

This type of lining had a life of from 4 to 6 weeks, during the latter part of which slabs of laminated refractory began to lift from the floor. Small pieces of oxide-impregnated refractory lodged in the channels, ultimately making cleaning impossible, and cracks in the channel blocks allowed metal penetration outward to the casing and inward to the transformer air tunnels.

The most prominent adverse characteristic was the gradual deterioration to a laminated lining structure, with slag and oxide penetration at the interlamination bands. General oxide penetration was fairly severe, and the linings did not give the desirable non-wetting characteristics.

(b) "Light-Stitch" Ramming

This method was adapted from German practice aimed at producing resilient, homogeneous envelope linings behind refractory-brick walls, as already described in connection with cast linings. Several linings of this envelope type were formed, but it was found that the combined construction, necessitating ramming behind brick walls, the upper parts of which had to be built during the ramming period, resulted in displacement of the "green" brickwork. Such linings were not only difficult to construct in twin-bath furnaces, owing to the restricted access in the vicinity of the transformer units, but proved unpredictable in regard to their capability for holding molten aluminium.

Hence, the "light-stitch" ramming technique was applied to the formation of a resilient monolithic lining against steel formers, the refractory-brickwork wall being omitted.

The lining material was spread in layers $1\frac{1}{2}$ –2 in. deep and rammed, using the maximum number of hammers that space would permit. On top of each stratum was left a $\frac{1}{4}$ -in. layer of loose refractory, which was criss-cross scratched with hand-tools to provide a bond between the successive layers. The general intention was to "stitch" the material together without the formation of well-defined strata, and to avoid

over-ramming the material to the maximum consolidation. All lumpy pieces of precompacted refractory displaced during the scratching operation were carefully removed before spreading each subsequent layer.

The total weight of rammed refractory was about 7 tons, and the lining was completed in about 40 hours' continuous work, including assembly and removal of the lining formers.

The lining produced by this method was intentionally much less dense than the flat-rammed linings, to give added resilience. The surface finish produced, using slightly oiled steel formers, was not so polished as with the flat-rammed linings, and small patches of almost open-grain structure were encountered in places throughout the lining.

Despite the efforts to avoid a stratified structure, the successive lining layers were clearly defined by narrow bands of coarse-grained refractory resulting from incompletely bonded cross-scratched material.

This lining had a life of 9 months, and finally failed owing to the shattering of the inner bath walls by flash-over in the transformer unit. During production there was a marked tendency to slag pick-up and oxide penetration, and the bath-wall material tended to pull away on cleaning, exposing the open-grain structure, which had to be sealed from time to time with a refractory cement wash. The most ominous feature was that the cleaning of the channels became extremely difficult, owing to build up of oxide and slag on the refractory-layer joints.

On breaking out the lining there was a distinct tendency for it to separate into the original layers, especially in the bath walls and upper channel block. Oxide penetration extended $1\frac{1}{2}$ –2 in. into the wall bases and 100% in the 3-in. channel walls.

Metal penetration had occurred vertically upwards into the channel block in flat veins, $\frac{1}{16}$ – $\frac{1}{8}$ in. thick, up to 5 in. wide, and up to 15 in. deep.

(c) "Heavy-Stitch" Ramming

This method of forming a lining was adapted from a technique observed during a visit to Germany, where it was applied to monolithic linings for single-bath, vertical-channel furnaces. The only variation was that the compacting hammer employed delivered 750 blows/min. at 80–90 lb./in.² mains pressure, compared with 2400 blows/min. used in Germany.

The compacting tools differed in design from those previously employed, the contact face being $1\frac{3}{16}$ in. long, with $\frac{1}{16}$ in. radius running into a 45° taper at the sides and ends. These tools were found extremely effective in compacting the layers rapidly with the minimum disturbance to adjacent material.

Refractory was added in layers 1 in. in depth, and the effect of the tools was to "V-stitch" or knit successive thin layers together into a dense homogeneous mass. This was aided by finishing each layer with rapid hammer runs which gave a closely serrated finish, but no scratching or chipping was done, and each successive layer was completed free of loose material and had the appearance of a dense clay mass.

The efficiency of this treatment was demonstrated in Germany when breaking out a lining of this type, which displayed a uniform density and an almost complete absence of stratification, except in the upper 12 in. or so of the walls, where the effects of secondary compacting were a minimum.

The time taken to form a lining of this type was slightly less than that for method (b) on account of the elimination of interlayer scratching, but the weight of material used increased to about 8 tons owing to compacting to the maximum density.

A lining of this type has now been in service for 32 months, and during that time has been employed largely for melting light-gauge material, including a high percentage of lacquer-coated or enamelled sheet, together with furnace skimmings and scalplings. The result of melting such material is to produce excessive quantities of oxide and dross, and an outstanding quality of the lining has been that over a long period it has maintained a surface having marked non-wetting quality, and a complete absence of visible layers. These features imply that oxide penetration into the now hard "fritted" surface of the lining is probably negligible.

The lining is extremely hard and has proved capable of withstanding considerable mechanical shock and wear. This may be due to the special technique applied to complete each layer, consisting of a run with a special hand-ramming tool held in contact with the lining formers. This contributed to the good surface quality by producing a skin layer about $\frac{1}{4}$ in. deep, with no sign of individual grains of the refractory and with an almost polished surface.

In the channels a $\frac{1}{16}$ -in. oxide skin was initially allowed to build up by making the cleaning tools $\frac{1}{8}$ in. less in dimensions than the rammed channel profile. This initial coating is essential to form a protective skin to resist the stresses and abrasions imposed during cleaning; cleaning at regular intervals has ensured that subsequent closure of the melting channels has been kept within limits which have not yet effected the electrical characteristics to any appreciable degree.

In general, although this type represents a departure from the idea of a non-dense resilient lining, its very hard and durable characteristics, in combination with the largely impermeable, non-wetting surface, have more than compensated for the slight additional heat loss incurred.

When melting certain types of scrap of various alloys, the furnace has to be completely drained for alloy changes, and the lining has not been adversely affected by the chilling and contraction which accompany this operation.

IV.—DESIGN PROBLEMS

1. FORMERS

Since, in the furnace under consideration, the melting channels are straight, it is possible to use collapsible metal formers in place of the wooden type employed

with more intricate channels, which are usually burnt away before drying out the lining.

The use of steel formers is preferable, wherever possible, on account of:

(i) The avoidance of absorption of moisture from the lining face, which would upset the very critical proportions that must be adhered to.

(ii) The additional rigidity obtained, which minimizes distortion and cracking of the already compacted mass, on subsequent ramming of additional material.

(iii) The smooth surface finish which results.

It is essential to ensure maximum rigidity of the formers, making the utmost use of bracing and joint flanges as stiffeners, and at the same time to maintain the maximum internal access for dismantling purposes. For the bath walls $\frac{3}{16}$ -in. plate has been found satisfactory and $\frac{1}{4}$ -in. unbraced plate is used for smaller box-like sections. The channel formers are assembled as a solid of the required cross-section from three components, each with the appropriate taper faces to permit collapse and withdrawal.

The formers have been designed to allow progressive assembly as ramming proceeds, thus permitting maximum access during formation of the lining, and avoidance of blind spots or severe restriction, which lead to faulty ramming.

The actual assembly proceeds as follows:

After ramming and levelling the floor of the furnace, the pre-assembled channel formers, channel-access-port formers, and lower bath formers, with associated thrust frames and anchor beams, are installed, and the plug-seating formers are attached from outside the shell.

When ramming has been completed to within a short distance of the top of these formers, the pre-assembled upper sections of the bath formers are added; this involves removal of the thrust frames and the anchor beams, the latter being subsequently refitted to the upper bath formers.

Provided that the pre-assembly work and floor levelling has been correctly carried out, the total time required for fitting the formers is 2-2½ hr., employing three men; this represents a considerable saving over previous former designs with separate channel formers which had to be individually anchored.

The assembly of the former components has been kept as simple as possible, to avoid waste of time during installation and removal. The arrangements are such that extraction pressures are well distributed over surrounding formers, or carried by spreader plates designed to conform to the lining profile. Where possible extraction pressures are transmitted directly to the furnace shell.

All component assemblies are dowelled, and the bolts are so placed as to be easily accessible for assembly or dismantling within the furnace, and at the same time to contribute the greatest possible rigidity to the structure. The design is such that the maximum pre-assembly work can be carried out and interruptions to the ramming reduced to a minimum.

The formers are designed to be anchored by heavy

cross-beams to the furnace-casing top flange, exerting a general downward pressure over the formers; this is a simple and robust arrangement.

The pull-down bolts are dowelled fits into blocks welded to the underside of the casing flanges; these blocks have been set by locating the whole former assembly before ramming the first lining. This means that the fitting of the formers requires only that the dowelled bolts shall register, and all that is necessary during ramming is a rapid check of the cross-centres with plumb lines.

The finish of the lining face of the formers is an important factor affecting the nature of the lining surface. The channel blocks, having been machined from solid material, present a good finish; the remaining surfaces are of mild steel plate, and these have been improved by light buffing.

Great care is taken to ensure that assembly joints present a flush outer surface, especially where collapsing strips are used, since any spaces in the former would leave ridges in the lining or "pull" the refractory during the removal.

The sequence of former removal, after completing the ramming, has been very carefully considered. In the design, since the damp rammed lining exerts quite a considerable grip on the formers, the maximum use has been made of extraction tools to withdraw collapsing strips, channel formers, small component formers, &c. The line of action of such tools is such as to avoid any surface pulling or lining fracture as far as possible, and they are usually in the form of draw bolts set into robust, welded housings. The use of discarded thrust races under the extractor nuts has been found greatly to reduce friction, improving "pull" without any corresponding increase of side thrust on the bolts.

2. FLOOR-LEVELLING PLOUGH AND FRAME

The ability to produce a plane floor, at the correct depth within the shell, is a vitally important factor in the production of a lining, since upon this floor are built the walls and channel block which depend for their solid, crack-free construction on the rigid seating of the lining formers.

The required floor level should be clearly defined by lines on the asbestos millboard covering the insulation brick walls, in conjunction with another line to which the plough frame is to be set.

The points which have been borne in mind in designing the frame and plough are as follows:

(a) The areas enclosed by the guide members of the plough frame must not, as far as possible, include any parts on which subsequent ramming is to take place.

(b) The frame should be of rigid construction to prevent deflection under the ploughs; in the present case, construction from 4 × 2-in. rolled steel channel has proved satisfactory.

(c) The hardwood plough beams must be of adequate depth to prevent sagging and be fitted with cast-iron bearing plates to "notch" over the plough frame, and mild steel strips along the ploughing edges.

(d) The setting and anchoring of the frame within the casing should be by means of wide hardwood wedges bearing against the insulation brickwork and the rammed floor.

V.—STEPS PRELIMINARY TO RAMMING

1. ASSEMBLY OF MATERIAL

Before preparing the wet refractory mix—and hence setting the time for beginning the lining operation—it is essential to ensure that all the accessory equipment is in serviceable condition and assembled on site. Having started ramming, protracted delays for whatever reason will obviously be to the detriment of the homogeneity of the lining. A site within easy reach of the furnace should be set aside for mixing the refractory and assembling the equipment in an orderly manner.

The equipment required will comprise: mild steel lining formers, extraction tools, ramming tools, and pneumatic hammers (with associated air hoses, receiver, moisture trap, &c.), plough frame and plough beams, roller-pan refractory mixer, refractory storage bins, weighing machine, gauge clocks, small hand-tools, buckets, and shovels.

The chief material requirements are: sufficient refractory material, supply of clean water, insulation bricks, asbestos millboard ($\frac{1}{16}$ in.), and silicate of soda.

It is recommended that the lining formers, which at this juncture should be pre-assembled to the first ramming stage of the lining, be installed in the furnace shell for a final alignment check relative to the trans-former unit. After removal, and immediately before use, the lining surfaces should be lightly wiped over with cotton waste saturated with a light oil.

In general, it must be stressed that all equipment should be in the cleanest and very best condition possible, to avoid any last-minute delays or improvisation leading to faulty work; again, meticulous attention to detail will be well repaid in the final results.

2. PREPARATION OF THE REFRACTORY

Before making the wet mix, the initial moisture content of the refractory material must be assessed. Samples should be taken from several of the supply containers, carefully mixed, and the final sample for test extracted. It is vital to ensure at this stage, and later, that no segregation of the fines from the quartz material takes place, and to this end the material should not be heaped in conical piles, because this practice results in the heavier material cascading down the sides.

In the work described here, the initial moisture content was 1.2–2.2%. This must be increased during wet mixing to give a content during ramming of about 5.2%, a proportion which ensures the minimum contraction after drying out consistent with the requisite compacting properties. Generally, however,

a moisture content of between 5.0 and 6.0% should prove satisfactory.

As a result of the handling the refractory receives from the time it leaves the mixer to its being spread in the furnace, a moisture loss of about 0.8% occurs. This is, of course, dependent on site conditions, and could be critical under adverse circumstances involving high ambient temperatures, shop draughts, &c.: this characteristic loss is offset by a comparable addition at the mixing stage.

The roller-pan type of mixer has proved satisfactory, and the machine employed has the following basic specification:

Stationary type, electrically driven at 20–25 r.p.m.

Pan 4 ft. 6 in. dia. \times 2 ft. deep.

Feed height 3 ft. 8½ in.; discharge height 10½ in.

Two kneading rollers, 22-in. dia. \times 8-in. face \times 300 lb., mounted on a spring-loaded yoke from the central drive pillar and offset from the radial axes.

Two adjustable ploughs on axis perpendicular to rollers, one feeding out from the centre, and one from the outside of pan into the path of rollers.

Two-gallon feed tank with distributor to pan, mounted on central post.

The method of feeding water into the mix is important in achieving the best results. Over-concentration of water in any part of the mix leads to the appearance of clay balls, and once these are formed they cannot easily be broken up and the moisture and fine clay redistributed, so that any batch exhibiting such characteristics should be scrapped.

The pipe from the feed tank is equipped with a valve to control the flow-rate and ends in a 4 in. \times 1½-in.-wide half-round trough, with six ½-in.-dia. holes evenly spaced. The trough is mounted 6 in. above and 4–5 in. in front of the convex plough blade.

The nature of the refractory is such that compacting occurs readily, and the rollers should be set to about 1½ in. above the pan base, so that the pressure exerted is merely sufficient to give a gentle kneading action without crushing or compacting the mix into cakes. This feature limits the batch for the pan size described to about 250 lb., which proves suitable for rapid and efficient mixing. The plough blades should be adjusted to give a nominal $\frac{1}{16}$ -in. clearance above the base, in order to prevent packing of the refractory or grinding of the quartz.

The practice is to spread out the refractory from the supply containers on to a clean, dry floor area, taking care not to permit segregation, or loss of fines by excessive handling or forming into conical heaps or high ridges. Having calculated the weight of water that must be added to a batch, each batch should be weighed out in suitable containers, such as buckets, and mixed according to the following procedure:

The mixer is started and the refractory charged with the minimum dissipation of fines.

The weighed quantity of water is charged to the empty feed tank and the control valve set so as to discharge it into the pan over a period of 1 min. (this setting should be previously determined).

The moisture is rapidly absorbed into the mix,

which changes in colour from light straw to brown, but after about 2 min. large, loosely compacted lumps tend to pile up in front of the plough blades. After another $1\frac{1}{2}$ min. or so the damp clay becomes more evenly spread through the batch, which takes on a finer and more uniform texture. A further mixing period of 1 min. is quite sufficient to ensure a satisfactory result, and the batch can then be discharged.

It is economical in time and labour to allow the machine partially to granulate the material by opening the discharge slide plate only about $1\frac{1}{2}$ in. and allowing the mix to be sliced out by the plough plates for a further minute or so, before finally opening the gate fully to scavenge the pan. All that is then required is to spread the batch about 1 in. deep and rub it over with the back of a shovel to break up any remaining loosely kneaded cakes. The batch should then be shovelled into one of the steeping bins. Again to avoid segregation, and also to ensure uniform retention of moisture, the batches should be roughly levelled off in the bins.

Batches may be mixed in rapid succession, the only delay being that necessary to remove any hard patches from the plough blades or pan, or any other accumulations of refractory. This material must on no account be used in the mix, but should be scrapped.

This cycle allows some 6 batches/hr. to be mixed, representing about 1500 lb. As each bin is filled with mixed material, it should be covered with damp sacks and numbered in order of mixing, so that the material may be rammed in the same order to ensure reasonably uniform steeping conditions.

By this mixing system the steeping time is considerably reduced from the 24-hr. minimum usually considered necessary. In an emergency, material has been rammed direct from the mixer without any detrimental results, although it must be admitted that such material has been used only in the upper few inches of the bath walls.

VI.—STAGES IN THE FORMATION OF A "HEAVY-STITCH" RAMMED LINING

It will readily be appreciated that it is of cardinal importance to ensure that every care is taken to maintain correct procedure during ramming, since one small unnoticed patch of carelessly rammed material, particularly in the region of the melting channels, may prejudice the life of the whole lining. Meticulous attention to detail by a good crew is therefore essential.

The actual formation of this particular lining may be broken down into the following stages. Stages (a)–(h) are illustrated in Fig. 2.

(a) Ramming the side gullies flanking the trans-former-housing base.

(b) Ramming the floor to the 4° slope required.

(c) Setting-in the plough frames and ploughing the seating areas for the formers to the correct level.

(d) Installation of the channel, cleaning port, and lower halves of the bath formers; anchoring into position.

(e) Ramming the channel block complete and bath walls to equivalent height.

(f) Installation of the centre-wall plates complete with pre-built insulation brickwork and fitting of upper halves of bath formers.

(g) Ramming the upper portions of the bath walls to complete the lining.

(h) Dressing the top surface of the walls to give the necessary clearance below the shell cover plates.

(i) Fitting of the bath shell cover plates.

(j) Removal of the lining formers.

(k) Fitting the lid rails and bath lids.

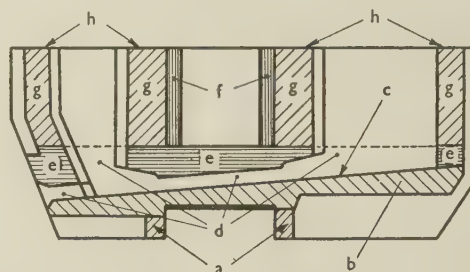


FIG. 2.—Diagram Showing Ramming Sequence.

The general ramming procedure is as previously described, applying 1-in. layers of refractory fully compacted without scratching or chipping.

Stage (a)

The side gullies are 7 ft. $4\frac{1}{2}$ in. \times 4 in. wide \times 9 in. deep, and should be rammed simultaneously to avoid any delay in starting the floor. The first layer, which is directly above the insulation brickwork, should be spread 3 in. deep, to cushion the hammer blows and avoid chipping of the brick. Any chips accidentally displaced should be removed. Subsequent layers are spread 1 in. deep and rammed up to within $\frac{3}{4}$ in. of the underside of the floor below the melting channels. The gullies should then be covered with damp sacking to prevent moisture loss before the remainder of the floor ramming is finished.

This stage should be completed with the furnace shell in the horizontal position and occupies about 1 hr.

Stage (b)

The furnace design requires a finished floor surface inclined at 4° to the horizontal, with a total area of about 60 ft.² and an average depth of 8 in.

Since the refractory brickwork base of the floor is built with a horizontal surface, it is necessary initially to build up the rammed refractory as a series of wedges, to achieve the 4° difference between the surfaces at least 3 in. before the final level is reached. The ramming can be carried out effectively only with the hammers held vertically; otherwise the pre-compacted material chips up. This also applies when compacting the initial layers on a hard, sloping base; to counteract this, the furnace should be back-tilted 4° to allow the floor to be finished in a horizontal plane.

It is necessary to maintain the furnace in this posi-

tion until the floor is finished and ready for the installation of the formers, &c., but it must be returned to the normal horizontal position for installing and finally checking the setting of the formers with plumb lines.

The ramming should proceed simultaneously on both bath floors, starting with an initial loose layer 3 in. deep to cover the refractory-built floor bases. It is as well to restrain the loose material when forming the initial wedge, by a row of moistened bricks placed across the floor. Subsequent wedge layers should be 3 in. deep where they extend over the bare floor, but should be thinned down to 1 in. over pre-rammed refractory. Layers are reduced to 1 in. as soon as all the base brickwork has a covering of firmly compacted material.

The thickness of each layer is gauged by the use of 1-in.-thick wooden blocks placed near each corner and at the centre of each bath floor. Loose material tipped into the working area is spread out using a straight-edge, and levelled by contact with pairs of gauge blocks. This method has proved the most satisfactory of those tried, and this is important, since the homogeneity of the lining depends upon even ramming, which presupposes that each layer receives an equal degree of secondary compacting from subsequent layers.

As soon as the bath floors have been covered, the ramming is extended over the gullies and the $1\frac{1}{2}$ -in. insulation brickwork flooring between the vertical-coil cooling ducts. The initial loose layer is, of course, 3 in. deep, and two subsequent layers, each 1 in. deep, are generally sufficient to link the two baths. The compacting of this part is most critical, since it forms the base of the channels, and great care should be exercised.

The refractory is then applied to complete the floor throughout up to the required level. Since the formers must be firmly and evenly bedded on smooth refractory, and since the final rammed surface does not comply with this requirement, it is normal practice to ram to about $\frac{1}{4}$ in. above the finished floor level. The excess material is subsequently removed by ploughing, to form a satisfactory level bedding surface for the formers. In the open areas forming the bath floors, a hard, close-grained surface is obtained by compacting with flat-surfaced hand-tools.

As soon as the correct level has been reached it is important to cover with damp sacking the areas on which the further portions of the lining have to be formed.

This stage of the installation normally represents about 6 hours' work, when using 6 hammers.

Stage (c)

The pre-assembled plough frame must now be lowered into the furnace, set to the required level, and firmly wedged in position.

In order to reduce the time spent in levelling the floors two plough beams are used simultaneously, with one man at either end of each beam applying even pressure and scraping the cutting face over the high floor

areas to accommodate the bases of the melting-channel and bath-wall formers.

All disturbed refractory must be removed before an accumulation interferes with plough movement, and in no circumstances must re-compacting of this material be allowed to take place; neither must such material be re-used anywhere in the lining.

Areas below the required level may be made up by scattering thin layers of refractory, say, $\frac{1}{4}$ -in. thick, to be rammed-in by rapid passes of the pneumatic tools. This ramming should not be carried out with flat hand-tools, as thin wafers of the material would be produced having unstable qualities and readily displaceable.

After ploughing has been completed, a careful overall check should be made before disturbing the plough frame, and this stage should normally be reached in $1-1\frac{3}{4}$ hr.

Stage (d)

Before proceeding any further, the furnace must be tilted back to the normal horizontal position, so that the floor takes on a 4° slope. The pre-assembled formers may then be swung into position and bedded down. It is advisable to sling the formers in such a way that the base line is also inclined at 4° , and will touch the floor simultaneously at all points.

The formers should then be lowered into the shell carefully, being finally inched down to allow the dowelled bolts to be inserted into the register blocks on the furnace shell.

During the subsequent bedding operations it is important to keep all the floor-bonding margins covered with damp sacks as far as possible.

An initial check must be made with an "inspection light" to ensure that no loose material is present between the formers and the floor, after which the formers should be allowed to stand with their full weight in position for several minutes.

Subsequent bedding consists of raising the formers about 4 ft. and scraping away all visible high spots and contact points. This is continued until full surface bedding has been achieved, small localized gaps of, say, $\frac{1}{16}$ in. under the bath formers can be tolerated, but it is essential to bed the channel formers all over. In this latter operation, it has proved satisfactory to scatter fine-grained refractory to fill low spots of up to $\frac{1}{16}$ in. deep, and to allow the weight of the formers to give the required degree of compacting.

Simultaneously with the final stages of bedding, centre-line wires should be set up between notches initially cut in the furnace shell, and, with suspended plumb lines, used to check the position of register marks on the channel formers.

Finally, the dowelled cross-beam bolts should be pulled down simultaneously to hold the formers on to the rammed floor.

The time required to carry out this stage is normally about $1\frac{1}{2}$ hr.

Stage (e)

Before continuing to ram the lining, it is necessary to re-tilt the furnace and bring the floor-jointing sur-

faces back to the horizontal. The ramming procedure is then as previously described, with 3-in. layers on initial surfaces and subsequent 1-in. layers.

To cover the channel and bath-junction formers, the ramming material is raised about $1\frac{1}{2}$ in. above their top surfaces on either side; the material is then rammed into the resulting depression, and thus prevented from sideways displacement.

A careful watch must be maintained at all times to see that excessive moisture is not given off at the pneumatic-hammer exhausts, as this may be sufficient to upset the moisture content of the mixture. Conversely, material should not be allowed to lie on the formers for any length of time, as this will rapidly dry, and, if included in the lining, would form weak patches.

The ramming should be carried on until the level of the top of the melting-channel block is reached, and this is finished with an extra $\frac{1}{4}$ in. at the sides to allow for the bedding of the bath centre-wall plates. Again, all exposed surfaces should then be protected with damp sacking. This part of the ramming takes 7-9 hr.

Stage (f)

Before installing the pre-bricked centre-wall plates, it is necessary to remove the anchor cross-beams. The wall plates should be lowered in and bedded down in a similar manner to the channel formers, to ensure firm overall contact when lined up with the frame bolts.

Pre-cut insulation bricks are built in to join the centre walls to the side walls, the new brickwork being then covered with $\frac{1}{16}$ -in.-thick asbestos millboard, using silicate of soda as the adhesive medium (see Fig. 3, Plate XLI).

The anchor beams and the thrust-extension frames previously bearing on to the lower halves of the bath formers having been removed, the upper halves of each bath former are installed, dowelled, and flange-bolted to the lower halves and the anchor beams refitted to bear directly on the upper halves.

The work of fitting these parts normally occupies 5-6 hr.

Stage (g)

The remainder of the lining can now be rammed by the usual method to within $\frac{1}{2}$ in. of the level of the shell top-cover plates surrounding the bath openings (see Fig. 4, Plate XLI).

It is important not to damage the asbestos millboard covering of the insulation brickwork when ramming the walls, and any flakes that become dislodged must be removed.

This final ramming stage usually occupies 8-10 hr.

It has been found that throughout the ramming of a complete lining the refractory wastage is approximately 4.5%.

Again it should be emphasized that finishing runs must be made with the hand-tools tight against the formers, at all stages, to achieve the highest-quality surface finish.

Stage (h)

The top horizontal surfaces of the bath walls can now be scraped smooth, to make the removal of subsequent metal splashes a simpler matter.

Stage (i)

The valanced shell top-cover plates should be fitted to protect the top surfaces and edges of the walls during removal of the formers.

Stage (j)

The removal of the formers may now take place and should be carried out to a systematic plan which should be rigidly adhered to. The formers should be removed as soon as possible after completion of the ramming, and any blemishes due to "surface pulls", &c., which show an open-grained structure should be closed by lightly tapping with a broad-nosed mallet. This stage should not be rushed and normally takes 6-8 hr.

Stage (k)

The remainder of the furnace fittings can now be fixed in position and the furnace lids so placed as to protect the linings from damage, but not to unduly restrict air circulation.

VII.—DRYING OUT AND COMMISSIONING THE FURNACE LINING

Drying out has been virtually broken down into two stages, the initial period, comprising air drying at shop temperature, and the second, consisting of raising the contained air and the lining to the temperature at which metal is to be introduced.

Hot-air drying has been tried for the initial stage from ambient temperature up to 150° C., but it was found that the extra expense and complication were not warranted by the advantages which accrued, in comparison with ordinary air drying.

During the air-drying period and while the lining is still "green", the transformer unit is installed and electrically connected.

The drying out, or firing, of the lining is most conveniently achieved electrically by reason of the fine control and uniformity of temperature that can be obtained. Elements of coiled wire carried on ceramic insulators are employed, mounted on frames of the appropriate shape constructed of heat-resisting steel.

In the baths a gap of 7-8 in. is left between the elements and the lining surface, and in each of the four channels the elements are mounted centrally and attached to, but insulated from, a $\frac{3}{4}$ -in.-dia. heat-resisting steel rod, which in turn is arranged at the correct height on ceramic bobbins.

It is considered essential to make the elements and frames as robust as possible, to reduce the chance of failure to a minimum, as element failures at the higher temperature ranges can result in severe chilling and involve the risk of lining cracks which may prove fatal.

The ratings of the elements employed were :

Charging bath	75 kW. at 400 V.
Offtake bath	65 kW. at 400 V.
Channels, each	6 kW. at 230 V. per pair

Each of these units should be separately wired into the power supply to permit its subsequent removal with power switched on to the remainder, and individually supplied with temperature-controlling and recording pyrometers. The melting channels are wired in pairs, since the thermal characteristics of the outer pair differ considerably from those of the inner pair; controllers are also coupled in this manner, but separate recorders are provided for each channel.

In all cases the recording and controlling thermocouples should be mounted with their tips as near together as is practicable, and securely attached to the

may open in the lining during air drying, close up owing to lining expansion between 400° and 500° C. In the rare occurrence of severe cracks wider than $\frac{1}{8}$ in., it may be necessary to "cross-brush" a cement wash into the opening; this, however, does not penetrate into the extremities, and there is a risk of further cracking due to leverage effects produced during any subsequent contraction. The merits of such a procedure must be judged according to the general condition of the lining.

One of the major problems common to all types of channel furnaces, is that of effectively drying out the channel walls without overheating and warping the coil-cooling air ducts. Premature use of the fan will retard the drying of the thin walls, and the introduction of metal before this is complete will precipitate cracking. The procedure found to be satisfactory is

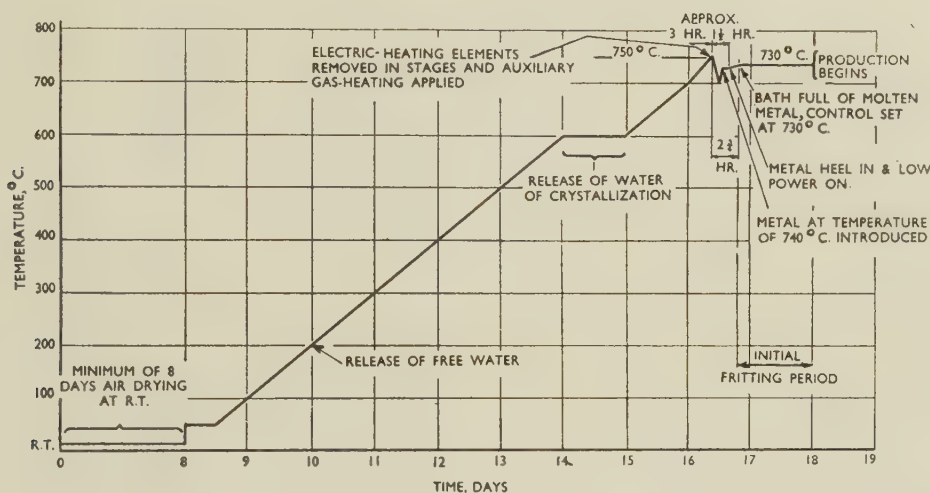


FIG. 5.—Sequence of Operations for Electrically Drying Out, Commissioning, and Initial Fritting of Rammed Monolithic Refractory Lining of 5.2% Free Moisture Content.

element frames or rods before installation in the furnace. The final position of the tips should be within 1–1½ in. of the refractory walls, and the longitudinal centre of the channels and 15 in. down from the top of the bath side walls, are found to be good positions giving stable results.

A further very advisable precaution is the provision of spare control couples, so that in the rare case of failure all that is necessary is to change over the wiring with the minimum fluctuation of temperature. Another practice adopted is to have a complete spare set of elements available, fitted with the necessary couples. Gas burners of an equivalent capacity should also be piped to the job for use during element removal, and in case of emergency.

It is important during the heating period effectively to seal off all air gaps in order to conserve the heat, as it has been found that leaks can cause severe thermal unbalance, particularly above 400° C. Specially cut asbestos-board discs are, for example, used to seal the channel-access ports.

It is found that any cracks up to $\frac{1}{8}$ in. wide, which

to allow the transformer-coil temperature to rise to 45° C., corresponding to a furnace temperature of about 500° C., before starting up the fan. The rise from 500° to 600° C., during which the water of crystallization is released, can then be successfully accomplished.

The following drying-out schedule has been devised with the object of satisfying the basic requirements of firing damp refractory and at the same time minimizing thermal shock (see Fig. 5).

(i) Air drying at shop temperature for a minimum of 8 days, with additional time if production commitments allow.

(ii) Raise rapidly from shop temperature to 50° C. and maintain for 12 hr. to achieve thermal equilibrium.

(iii) Raise from 50° to 100° C. in two stages of 25° C., with 6-hr. intervals.

(iv) Raise from 100° to 600° C. in even steps of 25° C. every 6 hr., i.e. 5 days' total.

(v) Maintain at 600° C. for 24 hr. to release the water of crystallization.

(vi) Raise from 600° to 700° C. in 24 hr., in two 25° C. steps with a 6-hr. interval and a final step of 50° C.

This latter allows a fairly long soak at 700° C. before charging of the molten metal.

(vii) Set controls up to 750° C. to create a heat reserve before removing the elements.

So far the drying out will have occupied a minimum of 16 days. This procedure and that for hardening out the surface and commissioning the furnace are in direct continuation and are illustrated on the graph in Fig. 5.

When commissioning, it is essential to maintain the temperature of the lining as uniformly high as possible, and this calls for the minimum delay in extracting the elements and introducing the molten metal. The first pots of metal, with sufficient volume to effect the hydrostatic seal over the channels, must be on site before the last element is cleared.

As soon as a uniform temperature of 750° C. has been achieved, the four ceramic plugs for sealing the channel-access ports should be prepared with jointing clay, and commissioning then proceeds as follows:

(1) Switch off power to, disconnect, and withdraw the central channel elements; then fit and secure plugs.

(2) Repeat for the outer pair of channels.

(3) Remove the offtake bath cover and introduce an auxiliary gas burner to maintain the temperature. Switch off power to, disconnect, and withdraw the heater element, taking care not to scrape the bath walls. Replace cover, leaving access for the gas burner. Instal and connect a thermocouple to the leads used for the element heater. Adjust the gas burner to maintain 730° C.

(4) Repeat this operation for the charging bath. In this case the temperature may fall as low as 700° C. when the large cover is removed, but should quickly rise again to about 720° C. on closure.

(5) Back-tilt the furnace by 4° to level the bath floor and thus reduce the volume of metal required to cover the channels.

Attach the pouring pot stands and the feed launder at the charging bath.

(6) Charge the first two or three pots, at 740° C., in rapid succession, to give a steady metal rise up the bath walls, and as soon as the channels have sufficient cover, switch on to the low-power tap. High power must not be used at this stage because of the heavier stresses which it imposes in the melting channels.

Ease off the gas burners to a setting that will maintain the temperature of the bath walls.

(7) Charge molten metal continuously and bring the level to 1½ in. below the top of the lining walls. The furnace should be tilted to the normal position during this stage.

The purpose of the high level of metal is to harden the upper walls, which, although not normally covered by the melts, are liable to mechanical damage.

As the metal level rises, the gas flames should be reduced and the burners finally removed before adding the last pot.

(8) The furnace should then be set to the required control temperature and allowed to stand for 48 hr. to enable the initial oxide skin to form on the lining. The power taps used during this stage should be of the lowest rating capable of maintaining the control temperature.

The time occupied for starting up is usually about 1½ hr. to switching the power on, with an additional 1¼ hr. before the bath is full.

In general, the installation and drying-out of these monolithic linings have been so arranged as to reduce mechanical stresses and thermal shocks to a minimum. In particular, the maximum temperature reached during the drying out was chosen to merge with the temperature of the molten metal when commissioning, and might be considered as rather low from the strict standpoint of refractory chemistry.

It was visualized, therefore, that the lining surfaces would not be fully hardened even after the initial 48 hours' fritting period. Consequently, during the first 2 weeks of production, special care is exercised during charging and when cleaning down the bath walls, and during this period the surfaces become satisfactorily hardened.

In any case, the melting channels should not be cleaned during the first week of production, in order that a ¼-in.-thick protective oxide skin may form and harden sufficiently to resist surface damage by the steel blades of the cleaning tools. To facilitate this, it is advisable to avoid charging scrap likely to introduce excessive oxide in the melts.

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THE USE OF REFRACTORIES IN LOW-FREQUENCY INDUCTION FURNACES FOR MELTING COPPER ALLOYS *

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SYNOPSIS

The attention which has been given to suitable refractory materials, and the improvements in techniques of lining construction and furnace operation that have been achieved, have contributed most importantly to the extended use over the last thirty years of the low-frequency induction furnace for melting copper and copper alloys. The advantages of melting such materials in furnaces of this kind are indicated, and an outline is given of those features of furnace design and operation which affect the use of refractories.

The types of refractory and methods of lining construction which have been found by experience and experiment to be best suited to the regular production of linings of satisfactory quality are then considered, and figures are given of the average life that has been obtained from linings used in the melting of deoxidized copper and the more important copper alloys.

The causes of lining failure are divided broadly into those connected with the construction and operation of the furnace, and those associated with reactions occurring between the refractory and the melt. Examples are given of the main types of furnace failure in each of these groups.

I.—INTRODUCTION

ALTHOUGH the low-frequency induction melting furnace originated over sixty years ago with the work of Colby and De Ferranti, and some early forms of this type of furnace, such as the Kjellin and Röchling-Rodenhauser, achieved a limited, though temporary, application for steel melting, it was not until the development of the Ajax-Wyatt furnace by Clamer and Wyatt during the second decade of the present century that it began to be used for melting copper alloys. Since then the Ajax-Wyatt and low-frequency induction furnaces of similar type, such as the Russ, have been increasingly employed for melting these materials, and today the major tonnage of brass alloys of all types, as well as nickel silvers, cupro-nickels, and to some extent deoxidized copper, for subsequent fabrication into such wrought forms as sheet, strip, tube, rod, section, and wire, is melted in furnaces of this kind. The benefits associated with this form of melting are considerable and now well known. They include high melting speeds, thorough mixing of the melt, low metal loss, low melting costs, simplicity of operation and technical control, and improved working conditions. As recently pointed out by two of the present authors,¹ the general adoption of the low-frequency induction furnace for melting copper alloys has been a major factor in achieving and maintaining a high standard of quality

in castings, and this, in turn, has been reflected in end products of more uniform composition and properties, of improved soundness, and greater freedom from non-metallic and other undesirable inclusions.

That it has been possible in little more than thirty years to extend successfully the application of the Ajax-Wyatt type of low-frequency induction furnace to the melting of so wide a range of important non-ferrous materials, with its attendant technical and economic advantages, is due largely to the attention given to the selection of suitable refractories for furnace linings, and to improvements in techniques of lining construction and operational details. These matters are of importance in all furnaces used for metal melting, but they have proved of particular significance in the industrial development of the low-frequency induction melting furnace. This is because of the peculiar difficulties associated with the production of refractory linings of the relatively complicated form characteristic of furnaces of this type, having the requisite combination of physical, mechanical, and chemical properties necessary to enable them to withstand the melting of large tonnages of material before replacement becomes necessary.

For some years after the advent of the Ajax-Wyatt furnace in the wrought copper alloy field, the linings used were such that it was possible to melt only brasses containing not more than about 70% copper. Even so, the tonnage that could be melted before

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relining became necessary was, by present standards, extremely low. In 1922 the average lining life of a 30-kW. furnace melting brass was quoted² as being about 75 tons and the maximum as about 375 tons. Furthermore, premature failure of linings was frequent. Today, linings are constructed, as a matter of normal routine, which can be expected, with a high degree of certainty, to withstand not only the melting of several thousands of tons of brass, but also large tonnages of copper alloys of higher melting point, for which, until recently, the low-frequency induction furnace was considered uneconomic because of the high cost of frequent lining replacement.

The purpose of the present paper is to outline the factors affecting the serviceability of refractories in

the design has remained basically unchanged. Sectional diagrams of single- and double-channel furnaces with melting capacities of 1000 and 2400 lb./hr., respectively—sizes extensively used today—are reproduced in Figs. 1 and 2. These furnaces comprise a refractory-lined cylindrical steel container, to the base of which is attached one or more assemblies, referred to for convenience as transformer units, wherein the heat used in melting is developed. That part of the furnace which forms the reservoir does not, under normal conditions of operation, present any unusual problems in refractory usage, and the greater part of the paper is concerned with the use of refractories in the transformer unit, since it is here that the main problems arise.

The transformer unit, illustrated in some detail in

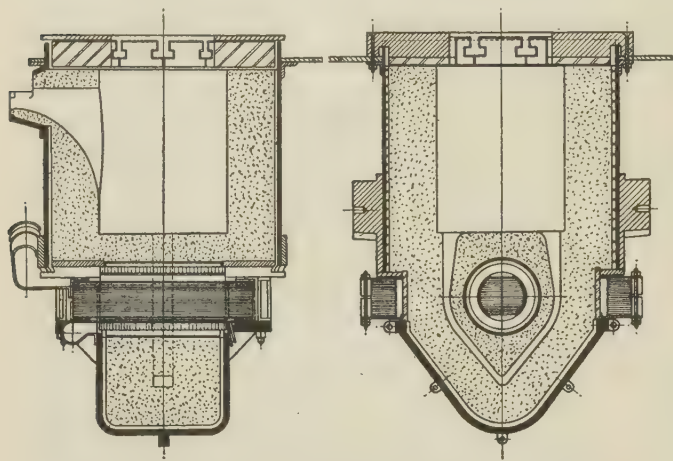


Fig. 1.—Cross-Section through Ajax-Wyatt-Type Low-Frequency Induction Furnace with a Single Transformer Unit.

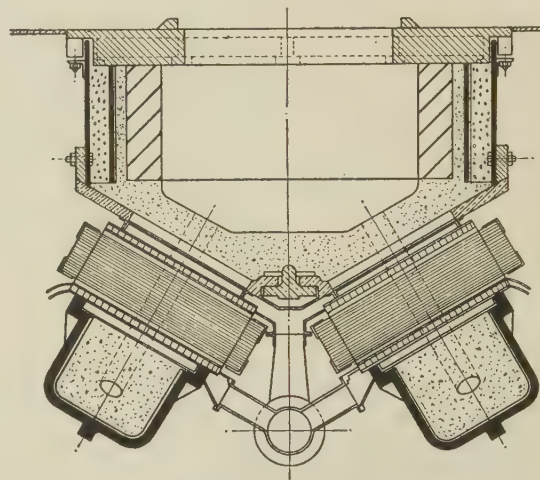


Fig. 2.—Cross-Section through Ajax-Wyatt-Type Low-Frequency Induction Furnace with Two Transformer Units.

low-frequency induction furnaces melting deoxidized copper and the more important copper alloys, to indicate the type of refractories and methods of lining construction found most suitable for this application, and to discuss the main types and causes of lining failure.

II.—DESIGN AND OPERATIONAL FEATURES AFFECTING THE USE OF REFRACTORIES

The Ajax-Wyatt low-frequency induction furnace is, in principle of operation, a step-down transformer, the heat utilized in melting being derived from electrical energy induced in the secondary circuit formed by a loop or ring of the metal being melted. While the design of these furnaces is directed to obtaining the maximum benefit from the "motor" and "pinch" effects, considerations of electrical efficiency necessarily impose onerous service conditions on the refractory in the channel area. Although furnace capacities have been increased substantially and there have been major improvements in speed of melting and in ancillary equipment,

Fig. 3, comprises essentially a refractory block with an open-ended secondary channel and central opening of relatively large diameter, in which the primary coil is located. The secondary channel is usually U- or V-shaped and has a cross-sectional area, depending upon the nominal electrical input of the furnace and the alloy being melted, of approximately 2.5–5.5 in.². In cross-section it may be circular, oval, rectangular, or a combination of these forms. The primary coil consists of about one hundred turns of flat copper tape wound edgewise, each turn being insulated. An annular space is left between the primary coil and inner surface of the refractory block, through which air is blown to prevent overheating of the coil and to cool the refractory. A metal earth shield is usually fitted in this space to protect furnace operatives from electric shock, and to minimize coil damage in the event of penetration to the coil of the molten metal. Alloy iron plates, usually of H section for convenience of assembly, forming the laminated iron core of the transformer unit, pass through the primary coil and around the outside of the transformer casing. The lower part of the latter customarily comprises two brass castings bolted together, and the

upper part, in the area of intense magnetic field, consists of thick insulating boards. The whole assembly is rigidly attached to the furnace-body casing, and normally the refractory lining of the transformer unit is continuous with that of the upper part of the furnace, although in certain types of furnace the transformer units are so designed and constructed as to make possible their separate replacement.

In operating these furnaces it is necessary at all times to maintain a sufficient depth of metal above the hearth to fill the channel or channels and thus complete the secondary circuit. This is achieved initially by priming with molten metal and thereafter at least sufficient metal to maintain the circuit is

such as asbestos, between the transformer casing and the refractory, dimensional limitations prevent this from being more than a relatively thin layer.

The efficient operation of the low-frequency induction furnace depends vitally upon the cross-sectional area of the secondary channel remaining substantially unchanged. This can only obtain if the refractory in which the channel is formed is not susceptible to spalling, i.e. cracking and/or flaking, and is resistant to erosion by, and chemically inert towards, the metal being melted, including metallic and non-metallic materials such as oxides which may be present in the melt. The high thermal gradient of approximately 1000°C. over a thickness of approximately $2\frac{1}{2}$ in. of refractory between the secondary

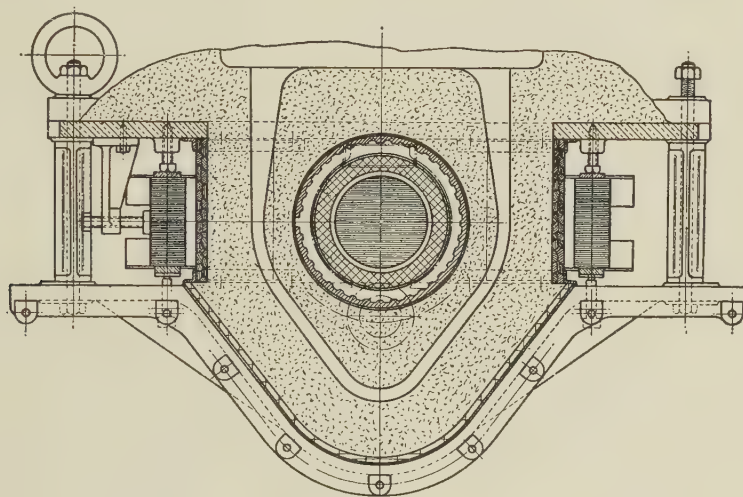


FIG. 3.—Cross-Section through Transformer Unit of Ajax-Wyatt-Type Low-Frequency Induction Furnace.

allowed to remain in the furnace after each heat has been poured.

The shape and dimensions of the refractory block in the transformer unit are determined within close limits by considerations of electrical efficiency. In order, for example, that a close magnetic coupling may be obtained between the primary and secondary circuits, the secondary channel is located as near to the primary coil as possible, the minimum distance varying with the size of furnace from approximately $2\frac{1}{8}$ in. in a furnace of 600 lb./hr. capacity to approximately $2\frac{1}{2}$ in. in one of 2400 lb./hr. capacity. The thinness of this refractory shell necessitates a high resistance to penetration by molten metal and metal vapour, if failure of the furnace due either to short circuiting between the primary and secondary circuits, or to metal leakage, is to be avoided. Also for reasons of electrical efficiency, a high electrical resistance is required. Again, because of the small thickness of refractory surrounding the molten metal in the secondary channel, the refractory must possess good heat-insulation properties if excessive heat losses are to be prevented, and while for this reason, it is common practice to insert a highly insulating material,

channel and cooled inner surface of the refractory block, provides conditions conducive to spalling. Should this occur, it would not only weaken the lining but, if it took place on the walls of the secondary channel, it might adversely affect the operation of the furnace through enlargement of the channel, or result in blockage of the channel and consequent failure of the furnace.

During melting, owing to a combination of "motor", "pinch", and "Joule" effects, considerable movement of metal takes place between the secondary channels and furnace reservoir, the effect of which is clearly apparent in the disturbed areas on the surface of the metal immediately above the secondary channel. From a consideration of the energy required to raise the temperature of a brass from 950°C. , its approximate liquidus temperature, to 1150°C. , the temperature at which the "pinch" effect manifests itself, it has been calculated³ that the metal in the channel is displaced at least 3.5 times/min. This represents considerable movement and indicates the erosive influences prevailing in the channel, which the refractory is required to withstand.

Since the whole of the heat utilized in melting is developed in the secondary channels, the temperature of the metal in these locations, and hence that to which the adjacent refractory is subjected under normal working conditions, exceeds that of the metal in the furnace reservoir. The temperature conditions in the secondary channels during melting cannot be readily determined. However, a number of experiments made by embedding thermocouples in the refractory block at various distances from the channel and estimating the temperature of the metal in the channel by extrapolation, have served to confirm measurements obtained by placing a thermocouple directly in the channel. In Table I are detailed

TABLE I.—*Approximate Pouring Temperatures and Estimated Maximum Temperatures to Which the Refractory Linings of Ajax-Wyatt Low-Frequency Induction Furnaces Are Subjected when Melting Deoxidized Copper and Various Copper Alloys.*

Alloy				Approx. Pouring Temp., °C.	Approx. Max. Temp. Attained in Secondary Channel under Normal Operating Conditions, °C.
Phosphorus-deoxidized copper				1250	1350–1450
Cu, %	Zn, %	Pb, %			
97	3	...		1210	1310–1410
90	10	...		1180	1280–1380
80	20	...		1140	1240–1275 *
70	30	...		1100	1140 *
63	37	...		1060	1090 *
58	40	2		1010	1070 *
Cu, %	Ni, %	Mn, %	Fe, %		
Bal.	5.5	0.55	1.2	1280	1380–1480
"	10	0.75	1.7	1320	1420–1520
"	30	1.00	0.7	1360	1460–1560

* Approx. "boiling point" of alloy under normal atmospheric conditions.

casting temperatures of a variety of copper alloys and an indication, from both measured and assessed figures, of the approximate temperatures to which the refractory walls of the channels in contact with the metal are subjected. For materials such as de-oxidized copper and cupro-nickel, which contain no appreciable amounts of volatile constituents, the temperature differential between the channel and the reservoir or main bath of the furnace is of the order of 100°–200° C. Thus, both in respect of erosion and temperature, the refractory constituting the channels is exposed to more onerous conditions than that forming the lining of the furnace body, which, as previously mentioned, does not present any particular or persistent problems. With alloys containing zinc, such as the gilding metals and the brasses, this temperature differential is not so great and decreases with increasing zinc content, ranging from about 100° C. or more for a 3% gilding metal to about 30° or 40° C. for brasses.

III.—TYPES OF REFRACTORIES AND METHODS OF LINING CONSTRUCTION

The design of the low-frequency induction furnace, particularly that of the transformer unit, the manner in which it operates, and the conditions obtaining in the furnace during melting, point to the following, apart from cost considerations, as the more important properties required of the lining :

- (i) Adequate refractoriness.
- (ii) Chemical inertness towards the melt.
- (iii) Low permeability.
- (iv) Erosion-resistance.
- (v) Resistance to spalling and cracking.
- (vi) Low thermal conductivity.
- (vii) High electrical resistivity.

1. TYPES OF REFRACTORIES

No one refractory having all these properties has yet been developed, and indeed only a limited number possess them to a degree sufficient to render them both economically and technically suitable for use in low-frequency induction furnaces for melting copper and copper alloys. These are refractories consisting mainly of silica and certain of the aluminosilicates. The compositions of two refractories extensively used are set out in Table II, together with an indication of their principal mineral constituents as determined by X-ray-diffraction analysis. The siliceous refractories, i.e. those containing approximately 90% silica, which comprise crushed and graded but uncalcined quartzite, usually admixed with about 15% uncalcined clay, are used mainly in the construction of linings of furnaces for melting phosphorus-deoxidized copper, cupro-nickel, and nickel silvers. The aluminosilicate refractories, which consist of a calcined, crushed, and graded fireclay base, possibly with some augmentation of the alumina content, with additions of 15–20% uncalcined clay, are employed extensively in furnaces for melting copper-zinc alloys and brasses containing small alloying additions of such elements as lead, tin, aluminium, &c.

Refractories of high alumina content, although very resistant to chemical reaction with most copper-rich alloys, have not been widely used, for their initial cost is relatively great and they are susceptible to cracking. Fused and ground magnesia of high purity, which is not wetted by most molten metals and has a considerable resistance to slagging attack, is not normally used in low-frequency induction furnaces for melting copper and copper alloys because of its high cost and susceptibility to spalling.

2. LINING CONSTRUCTION

Of the many methods of lining construction investigated and practised at various times, that best suited to the regular production of uniformly high-quality linings is by ramming the moistened powdered refractory within the furnace casing into a so-called

"monolithic" block, about formers of appropriate shape and size. Although simple and convenient, this method of construction requires the exercise of considerable care, particularly in regard to the conditions prevailing during ramming, the grading, moistening, and mixing of the refractory, the manner in which the ramming operation is conducted, and the drying of the rammed lining before use.

Because of the possibility of damage to the completed lining in transportation, the lining operation should preferably be carried out adjacent to the position in which the furnace is to be used. Precautions must, moreover, be taken to avoid contaminants from atmospheric or other sources entering

at the base of the cone. For machine-mixing, a horizontal fixed cylindrical drum with blades rotating about a horizontal axis is employed, the required quantity of refractory being emptied into the drum and the moistening agent added slowly, again through a fine spray.

To obtain consistent and reproducible results, the refractory mix at the time it is made must have a moisture content of about 6%. Accurate control can be effected by the use of a moisture meter; this method is preferred to judging when the correct amount of liquid has been added by squeezing some of the mixture in the hand and assessing its strength by pulling it apart. Since the actual ramming

TABLE II.—*Approximate Chemical Composition, Principal Mineral Constituents, and Grading of Two Typical Refractories Used in the Construction of Linings of Ajax-Wyatt Low-Frequency Induction Furnaces Used for Melting Phosphorus-Deoxidized Copper and Various Copper Alloys.*

Chemical Composition of Dried Refractory and Principal Mineral Constituents			Physical Characteristics of Dried Refractory		
	Siliceous Refractory	Alumino-Silicate Refractory		Siliceous Refractory	Alumino-Silicate Refractory
SiO ₂	% 88.6	% 54.1	Particle-Size Distribution, % :		
Al ₂ O ₃ (combined)	5.6	38.3	+ 6 B.S.S. mesh	25.8	nil
" (free)	1.0	1.2	12 " " " "	9.2	0.9
Fe ₂ O ₃	0.9	1.3	25 " " " "	4.5	19.8
TiO ₂	0.4	1.9	44 " " " "	3.8	12.8
CaO	0.8	0.3	60 " " " "	5.7	5.7
MgO	0.1	0.1	100 " " " "	10.6	5.5
Na ₂ O	0.6	0.6	200 " " " "	12.6	8.6
K ₂ O			—200 " " " "	27.8	46.7
Loss on ignition	2.0	2.2	Apparent Density (after consolidation by tapping), g./c.c. . . .	1.79	1.80
Principal mineral constituents as determined by X-ray-diffraction analysis	α-quartz; α-cristobalite	mullite; α-cristobalite; α-quartz	True Density, g./c.c.	2.55	2.76
			Powder Mass Porosity, %	29.8	34.8

the lining during construction, since these may impair its performance by acting as fluxes or giving rise to areas of local weakness. The refractory is usually supplied "dry" and requires the addition of water to yield a mixture of workable consistency. Too little moisture results in insufficient bond strength and plasticity, while too much produces a mix which "flows" from under the hammer during ramming. Furthermore, excess moisture may cause undue contraction, and consequently cracking of the lining during drying. Distribution of water evenly throughout the mass of the refractory is essential, and for this reason machine-mixing is preferred to hand-mixing. Moreover, it reduces the risk of segregation of the various-sized particles. Whichever method is adopted, the refractory is first passed through a $\frac{1}{4}$ -in.-mesh sieve. In hand-mixing all the refractory material required is sieved into a flat-topped heap on a carefully cleaned area of iron-plated floor, and the moistening agent added in small quantities through a fine spray, the mixture being turned by shovel until a fine, even distribution has been achieved. The formation of a conical heap of refractory at any time during the process is to be avoided, since this tends to result in the segregation of the coarser particles

operation may take up to 10–12 hr., during which time the moisture content would change considerably owing to loss by evaporation if the refractory were left exposed to the atmosphere, the moistened refractory is transferred immediately after mixing to air-tight containers from which only such quantities are withdrawn for ramming as can be used within a short period.

Hammers are used for ramming, operated either pneumatically at a pressure of 80–90 lb./in.², or electrically. Although the latter are claimed to be more uniform in operation, satisfactory results are obtained with the air-operated hammer if precautions are taken to avoid condensation of water in the pipeline; this, if it occurs, affects the pressure and hence the power of the hammer, and may, if carried into the hammer itself, be ejected on to the surface of the refractory, with consequent damage due to the formation of local areas of high moisture content. The hammers consist usually of a flat, rectangular steel head on a round shaft of suitable length. Hammers with different sizes of head are needed during the ramming of a furnace, a head approximately 3 × 2 in. being used for most of the work and one of 2 × 1 in. for those areas more difficult of

access. The blow imparted by the hammer is considerable, and it is essential therefore that the various parts of the furnace casing and the formers, as they are put in, should be rigidly mounted to avoid cracking of the lining.

Wooden formers are used for producing the secondary channels, the central hole in which the primary coil is located, and the inner contour of the furnace body. The secondary-channel former is usually a hollow wooden pattern through which may be threaded a strip of nickel-chromium alloy or other suitable material; by resistance heating this can be used to burn out the former and dry the refractory surrounding the channel after the lining has been completed. The outer surface of this former is treated with a material impervious to water, such as shellac, to avoid swelling or warping of the wood and resultant damage to the lining which would occur if moisture were absorbed from the refractory. A cast-metal channel former⁴ has a number of important advantages over the conventional wooden former. For example, if it is so constructed that the upper ends of the channel are connected together with metal, the former itself can be heated by induction from the primary circuit of the furnace. By suitably controlling the input to the primary coil the temperature of the secondary channel can be maintained, if necessary for long periods, at a low value for drying out the lining and later, by increasing the input, it can be raised and the metal ultimately melted.

Ramming is carried out in successive stages, at each of which only a relatively small quantity of refractory is consolidated. The optimum amount of refractory for ramming at each stage has been found to be such as to produce a hard rammed layer approximately $1\frac{1}{2}$ in. thick. The moistened refractory is first consolidated by hand and then rammed with pneumatic or electric hammers until a hard, dense layer is formed, the hammer being worked slowly backwards and forwards over the whole surface. When, as is the usual practice, two operatives are engaged at one time, they work in unison and ram symmetrically about an imaginary centre line to ensure uniform treatment of the refractory. In this method of construction the interface between successive layers of rammed lining is a source of potential weakness, and metal penetration at these interfaces is liable to occur unless a satisfactory bond is obtained. This is achieved by breaking up the surface of the hard rammed layer thoroughly to a depth of approximately $\frac{1}{4}$ in. with a pronged iron tool and carefully removing and discarding the whole of the loosened refractory before making the next addition. Moistening of the roughened surface before addition of further refractory is not recommended, since this results in variations of moisture content throughout the lining, with consequent risk of distortion and cracking during drying or heating. Once construction of the lining has begun, it is, if possible, continued without interruption until completed, to avoid the excessive loss of moisture which would

occur from leaving the surface of a partially built lining exposed, and the resultant inferior bond at this position. If, for any reason, work has to be discontinued, the exposed surfaces so far completed are protected by damp sacking.

The sequence of operations in forming the rammed lining of a low-frequency induction furnace of 600/1000-lb. capacity with a single transformer unit is initially to line the transformer-unit casing with a layer of heat-insulating material, which may be firebrick or asbestos sheet depending on the amount of space available, and then to ram the refractory in layers until a level is reached corresponding to the bottom of the furnace-channel former. This is then rigidly clamped in position and ramming continued, particular care being taken to ensure that the refractory at the base of the channel is consolidated, until the lower level of the primary-coil opening is reached. The cylindrical wooden primary former, on which is mounted the metal earth shield wrapped with a thin sheet of asbestos, is then placed in position and ramming is continued to complete the transformer unit and form the hearth, after which the outer casing and wooden body former are inserted. Ramming is continued between this and the outer casing until the whole lining has been completed. Various stages in the construction are illustrated in Figs. 4-12 (Plates XLII and XLIII).

This sequence is modified when, as may be convenient and economic in the construction of linings of fairly large-capacity furnaces, a pre-fired refractory ring is used to form the body lining. After the transformer unit has been rammed and fixed to the body casing, the hearth is completed and the body ring lowered into position, a liberal quantity of fire-clay cement being used to form a joint between the two. The annular space between the body ring and furnace case may be rammed wholly with the normal ramming mixture in the conventional way or, to avoid unnecessary use of this relatively expensive material, the space may be partially rammed with the normal mixture and partially filled with broken firebrick and similar refractory rubble. If the latter technique is adopted a steel sleeve is inserted to divide the space between the refractory body ring and furnace casing and the ramming mixture is confined to the area between the body ring and steel sleeve, and the fireclay rubble to that between the sleeve and casing.

The transformer unit may be built separately, either in a manner similar to that just described, with the rammed layers perpendicular to the axis of the secondary channel, or by "side ramming", when the layers are parallel to the axis of the secondary channel (Fig. 13, Plate XLIV), and incorporated into a complete lining after drying by ramming in the normal way. Such a technique enables the drying of these relatively small blocks of refractory to be carried out under carefully controlled conditions over longer periods than would usually be convenient for a complete furnace.

The construction of low-frequency induction furnace linings by ramming the refractory in a succession of relatively thin layers, as stated earlier, has the disadvantage that the interface between successive layers presents a potential source of weakness. Attention has therefore been directed for many years to developing methods of construction, particularly of the transformer unit, free from this disadvantage. At various times, from as far back as the early 1920's, trials have been conducted on furnace linings in which the transformer unit has been constructed separately and pre-fired before being built into the furnace. Units so produced have generally proved unsatisfactory, either because of extreme porosity or because of the presence of hair cracks—defects which can usually be detected by closing one end of the secondary channel, introducing coal gas under slight pressure at the other, and examining the outer surface of the block for gas leaks. Another method of construction now being evaluated is that of using pre-fired refractory tubes,⁵ examples of which are shown in Figs. 14 and 15 (Plate XLIV), to form the secondary channel. These tubes are incorporated in the slot unit during construction in much the same way as the wooden channel former which they replace. They are available in a range of refractory materials such as sillimanite, alumina, and silicon carbide, in shapes and sizes suitable for forming the channel of low-frequency induction furnaces. Tubes with a wall thickness of 1 in. are sufficiently robust not to be damaged during the ramming of the refractory with which they are backed.

3. DRYING AND PRIMING

The freshly rammed lining contains a considerable amount of moisture which has to be removed without the development of cracks which could arise from uneven contraction of the lining as a result of too rapid drying of the surface, and from the generation of high internal pressures consequent upon the too rapid evaporation of the moisture. Ideally, the lining should be maintained until dried at about 120° C. in an atmosphere the humidity of which is gradually reduced from saturation to zero. Such conditions, however, would be both costly to provide and inconvenient to use for complete furnace linings, and it has been found by experience that drying can be carried out satisfactorily by allowing the furnace to stand either in a relatively warm building or in a cabinet maintained at about 100° C., preferably for a period of not less than two weeks. At the end of this time the channel former is burnt out slowly with a gas torch or by electrical-resistance heating.

Before priming the furnace with molten metal, the temperature of the channel is raised to approximately 1100° C., to prevent the refractory from being subjected to thermal shock when molten metal is introduced and also to effect some fritting of the refractory near the channel surface. The rate at which the channel is raised to the desired temperature

is carefully controlled in order to avoid the development of cracks. A gas-fired torch is satisfactory for this purpose, and for the first 24 hr. gas only is used, the amount of air being gradually increased over the next 36 hr. to produce at the end of that time the required temperature, which is then maintained for at least 12 hr. During this period the body lining is also heated by the insertion of a second gas torch, particular care being directed to preheating the hearth to reduce the risk of damage to this part of the furnace when metal is introduced. Generally it is convenient and satisfactory to prime furnaces with a similar alloy to that on which they are to operate, but those to be used for melting alloys such as cupro-nickels and nickel silvers are preferably primed and operated for a short period with deoxidized copper and brass, respectively, metals which are less severe in their attack on the linings.

IV.—LINING LIFE AND CAUSES OF LINING FAILURE

1. LINING LIFE

The life of the lining of an Ajax-Wyatt low-frequency furnace is usually expressed as the tonnage of metal melted before the lining becomes unserviceable. This provides a satisfactory basis for comparing the performance of linings of furnaces of similar size which have operated under approximately the same conditions, particularly in respect of materials and speed of melting. It is not unusual, in industrial melting, for alloys differing significantly in the severity of their attack on furnace linings to be melted in one lining during the course of its life, and indeed an alternation of materials melted is sometimes deliberately practised to prolong furnace life. The temperature conditions obtaining in the furnace during melting depend largely on the melting rate and, other things being equal, the life of linings decreases with increased speed of melting and vice versa. It has also been found, particularly in brass melting, that the average lining life increases with furnace capacity. For example, the average life of linings used for melting brass in furnaces of 2000-lb. capacity is nearly four times that of linings used for melting the same materials in furnaces of 1000-lb. capacity. In Table III are set out the average and maximum tonnages obtained over a number of years from linings of furnaces melting deoxidized copper and various copper alloys. They relate only to linings used for melting materials of substantially the same composition.

Failure of low-frequency furnace linings is due almost invariably to occurrences in that part of the lining in which the secondary channel is located, the types of failure most commonly encountered being an appreciable increase or diminution in the cross-sectional area of the channel, formation of local constriction in the channel, or penetration of metal

through the lining to the primary coil or outer casing of the transformer unit. An indication of the relative incidence of the different types of failure experienced is given in Table IV.

It not infrequently happens during the life of a furnace, which may be of several years' duration, that

lining lives illustrated graphically in Fig. 22, and consequently to the large disparity between the maximum and average life of furnace linings. Where there is little tendency for the refractory and melt to react, as in the melting of 70 : 30 brass, failure most commonly arises from constructional or operational

TABLE III.—*Tonnage of Phosphorus-Deoxidized Copper and Various Copper Alloys Melted in Low-Frequency Induction Furnaces Before Relining Becomes Necessary.*

Principal Alloy Melted	Approximate Composition					Nominal Capacity of Furnace, lb.	Lining Life, tons		Type of Refractory Used
	Cu, %	Zn, %	Pb, %	Al, %	Sn, %		Average	Max.	
Phosphorus-deoxidized copper	1000	441 262	2600 808	Siliceous Alumino-silicate
Brasses and gilding metal	1000 2000	1530 5320	9140 24,900*	" "
Leaded brass	58	40	2	2400	2939	8996	" "
Aluminium brass	76	22	...	2	...	2400	1278 †	1791 †	" "
Tin brass	70	29	1	2400	1533 †	2048 †	" "
Nickel silver	1200	165	321	Siliceous
Cupro-nickel	2200	103	323	"

* Furnace still in operation.

† Total output from these furnaces was much higher owing to the substantial quantities of other alloys being melted.

a number of factors have contributed, independently or simultaneously, to deterioration of the lining, so that it becomes a matter of uncertainty which has been the most potent. These factors can be divided broadly into those connected with the construction

TABLE IV.—*Principal Types of Failure of Low-Frequency Induction Furnaces Used for Melting Phosphorus-Deoxidized Copper and a Number of Copper Alloys.*

Type of Furnace Failure	Principal Alloy Melted				
	Phosphorus-De-oxidized Copper	Brass and Gilding Metal	Leaded Brass	Nickel Silver	Cupro-Nickel
Penetration of metal from secondary channel or hearth to primary coil or transformer-unit casing	45	49	39	84	97
Enlargement of secondary channel		3	...		
General diminution in cross-sectional area of secondary channel	...	3	49
Local constriction in secondary channel	41	3
Miscellaneous causes	14	42	12	16	3

and operation of the furnace and those associated with reactions occurring between the refractory and the melt.

2. FAILURES ASSOCIATED WITH LINING CONSTRUCTION AND FURNACE OPERATION

It is the fortuitous incidence of factors associated with the construction and operation of low-frequency induction furnaces that gives rise to the very variable

faults, whereas in melting cupro-nickel failure occurs usually as a result of this reaction.

Many details of procedure in lining construction and preparation for service, if carried out incorrectly, can lead to, or contribute towards, lining failure. As mentioned earlier, the commonest of these are incomplete bonding of adjacent ramming layers, inadequate ramming of the refractory, too rapid drying of the lining after construction, and an excessive difference in temperature between the lining and melt when the furnace is primed. An example of the penetration of metal at the junction of the ramming layers in a furnace used for melting leaded brass is shown in Figs. 16 and 17 (Plate XLIV). The effect of loosely rammed refractory immediately below the secondary channel, where uniform ramming is most difficult to accomplish, is either to facilitate metal penetration through the lining or to cause a local collapse of the channel wall and consequent blockage. The result of too rapid drying or preheating of the lining, or its subjection to severe thermal shock as a result of insufficient preheating before priming, is the development of cracks through which metal may penetrate either to the primary coil or to the outer casing.

The most satisfactory procedures for the operation of low-frequency induction furnaces for melting copper alloys are now so well established and maintained that lining failures due to operational causes are much less prevalent than formerly. Improvements that have made valuable contributions to increased lining life have been the standardization of methods of furnace charging, the adoption of controlled melting rates, the introduction and use of temperature control during melting, and adequate attention to the operations of fluxing, skimming, pouring, and furnace cleaning.

A frequent cause of lining failure associated with operational technique is penetration of metal through the hearth of the furnace on to the primary coil, an example of which is illustrated in Fig. 18 (Plate XLV). This arises from damage to the hearth caused by charging of massive raw materials or scrap,

frequently in furnaces with two transformer units, since these are situated on either side of the centre of the hearth, where maximum damage to the lining occurs, and the hearth itself is thicker than in smaller furnaces. Furthermore, the design of these furnaces is such as to permit the repair of a damaged hearth without the necessity for a complete rebuilding of the lining.

The adoption of controlled melting rates, which vary with furnace input and type of material being melted, is necessary to ensure that an excessive temperature does not develop in the secondary channel at any time during the melting cycle. Should this occur the life of the lining may be seriously impaired, since many of the chemical and physical actions which take place in the secondary channel do so more rapidly at elevated temperatures. Furthermore, the introduction of temperature control during melting has additionally improved the quality of castings and reduced metal loss.

Furnace linings are severely attacked and their life adversely affected by certain fluxes sometimes used in melting. A notable example is borax, the effect of which is not only to cause severe attack on the refractory lining the reservoir, but also on that in the channel itself.

The dross which builds up on the walls of the reservoir is removed periodically by means of a steel bar, commonly known as a pecking bar. This again, is an operation which, if not carried out carefully, may result in severe damage to the relatively soft refractory lining of the reservoir. At one time it was the practice to use this or a similar pecking bar to clear deposits from the walls of the secondary channel, but a growing appreciation of the risk entailed of damage to the channel walls has resulted in its being discontinued, except in the case of a local blockage when a bar must be used to try to remove the obstruction.

To avoid unnecessary consumption of electricity by maintaining furnaces on stand-by loads over periods when they are not in production, the practice of allowing metal to solidify or "freeze" in the furnaces has been increasingly adopted. This introduces another hazard, and lining failures were quite frequent before a suitable procedure involving most careful control of the cooling and reheating operations was devised. Nowadays such failures are relatively unusual; for example, one furnace melting leaded brass is recorded as having been frozen and remelted no fewer than 190 times. The cause of furnaces failing to restart after freezing is usually a fracture of the secondary loop, such as that illustrated in Fig. 17 (Plate XLIV), brought about by contraction stresses set up during the cooling cycle. The risk of this happening has been largely eliminated by ensuring that the metal freezes progressively upwards from the lowest part of the channel. To achieve this, the amount of metal in the furnace is first reduced to leave a bath of approximately 5-6 in. in depth. Oxide and dross are then skimmed off and a layer of charcoal approximately 12 in. thick added, after which the metal is heated to

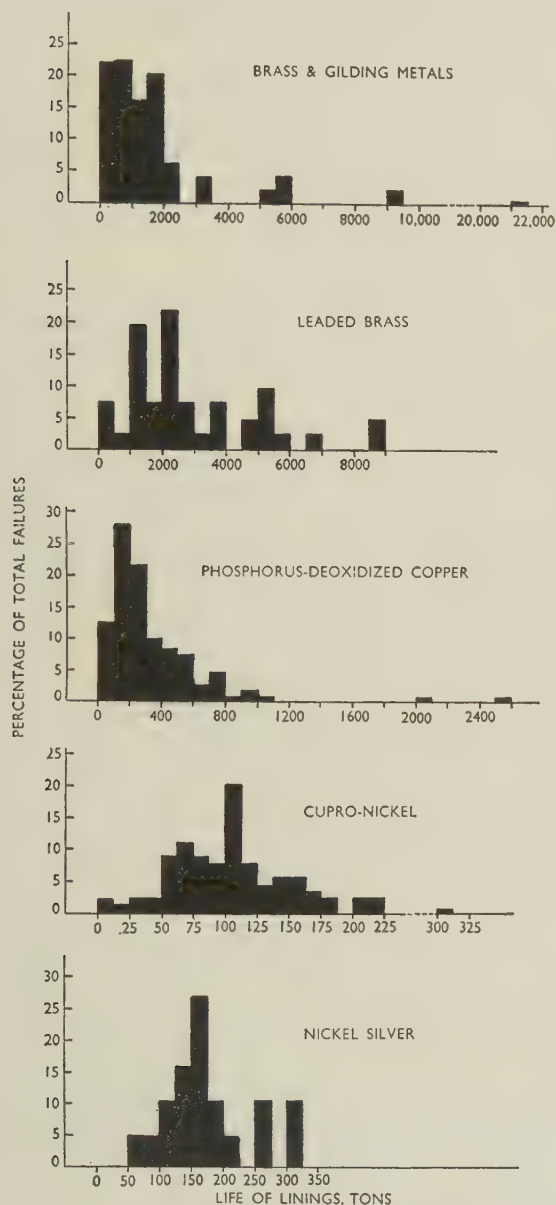


Fig. 22.—Incidence of Lining Failure in Ajax-Wyatt-Type Low-Frequency Induction Furnaces Melting Deoxidized Copper and Copper Alloys.

particularly when there is only a relatively small amount of residual metal in the furnace after a heat has been poured. Damage of this sort can largely be avoided by introducing light scrap into the furnace before the more massive portions of the charge. Lining failures due to hearth penetration occur less

normal pouring temperature. When freezing furnaces which have V-shaped secondary channels, the fan supplying air for cooling the primary coil is then switched off and finally the power to the furnace itself, this sequence being necessary to prevent fracture of the metal in the secondary channel during cooling. The procedure is modified when freezing furnaces with U-shaped channels by allowing the cooling fan to remain in operation until the furnace is cold. To remelt, the coil-cooling fans are brought into operation and the furnace put on the lowest stand-by load necessary to maintain the metal molten under normal working conditions. After approximately 8 hr., the whole of the metal in the channel and the bath will have melted, when normal operations can be resumed.

3. FAILURES RESULTING FROM REACTIONS BETWEEN THE REFRACTORY AND MELT

Chemical action between the refractory and the melt, and the nature of the resultant product, represent important factors affecting the life of low-frequency induction furnace linings. Such reactions usually occur between constituents of the refractory material and metal oxides. As might be expected, the extent to which they proceed and their consequent harmful effect on lining life is most marked in and around the secondary channels, where movement of molten metal is most vigorous, hydrostatic pressure is greatest, and the highest temperatures obtain. These reactions are varied and sometimes complex, and their precise nature is difficult to determine. Moreover, the conditions believed to prevail in the furnace channel during normal furnace operations cannot readily or accurately be reproduced for study in laboratory experiments. Nevertheless, investigations, including petrological examination, chemical analysis, and porosity determination after service on specimens of furnace linings prepared by ramming in the manner described earlier, and of laboratory samples of refractories exposed to the action of molten metals and metal oxides under various conditions, have provided some indication of the mechanism of lining deterioration by chemical action.

Under the hydrostatic pressure exerted by the metal in the furnace reservoir, some of the metal in the secondary channel penetrates into the interstices of the refractory surrounding the channel. This penetration may extend to a depth of an inch or so and is halted by the combined effect of oxidation of the metal by air in the pore structure of the refractory and by solidification of the metal. In the affected penetrated area surrounding the secondary channel a number of well-defined and often strongly coloured zones can be distinguished, in some of which the refractory has undergone substantial chemical and physical change.

The refractory adjacent to the metal, except where selective slagging attack has occurred, consists of a zone of low porosity and correspondingly low permea-

bility. This contains finely dispersed unoxidized metal and under certain conditions slag also. Surrounding this is a zone of higher porosity, in which is present infiltrated metal, lacking the globular form of that in the inner zone, and increasingly oxidized towards its outer boundary. Between this and the substantially unchanged refractory is a zone in which the interconnected porosity is completely filled with metal oxides.

Any interaction between the refractory and metal oxides is not restricted to the metal/refractory interface, i.e. the walls of the secondary channel, as a result of the presence of the metal oxide in the melt itself. In so far as the temperature conditions are favourable, it can also take place within the lining immediately surrounding the channel owing to the presence of metal oxides there also.

If the reaction product is fluid it is removed from the channel walls, and with consequent enlargement of the channel there is a corresponding change in the temperature conditions in the remainder of the lining. This causes oxidized metal at a greater depth to react with the refractory to form isolated deposits of slag and oxide-free metal, while metal oxide in what had previously been the outer zone, referred to above, also reacts to form liquid slag. The latter reaction permits molten metal to penetrate the oxide barrier into the hitherto unpermeated refractory, until this process is again halted by the combined effects of oxidation and solidification. The depth and character of the penetrated zones are thus maintained as the secondary channel becomes enlarged.

The melting of cupro-nickel and nickel silver in siliceous refractories is accompanied by the formation of a fluid reaction product. This is due to the presence in these alloys of manganese, the oxide of which reacts readily with silica to form the eutectic $\text{MnO} \cdot \text{SiO}_2 + 2\text{MnO} \cdot \text{SiO}_2$. The reaction proceeds more rapidly with the cupro-nickels because of the higher temperatures to which these alloys are heated during melting, and also because of their higher manganese content. It is not unusual for the cross-sectional area of the secondary channels of furnaces used for melting cupro-nickel to increase in area from approximately 5.5 in.², as initially constructed, to approximately 35 in.² by the time the furnace is taken out of commission because of excessive current consumption or thinness of the lining between the secondary channel and outer casing. The condition of the siliceous lining in a twin-channel, Russ-type low-frequency induction furnace after melting approximately 200 tons of cupro-nickel is shown in Fig. 19 (Plate XLV).

When the action between metal oxides and the refractory is selective in character, that is, when one oxide of the latter is preferentially attacked and the resultant product is fluid, the oxide-impregnated and adjacent zones in the lining surrounding the channel are similar in character to those previously described, but the refractory immediately adjacent to the channel wall becomes extremely porous and the pores are filled with metal. In this condition the

refractory is highly susceptible to erosion by the moving metal in the channel and eroded refractory can accumulate in the lower portion of the channel in sufficient quantities to cause blockage and rupture of the secondary circuit. Linings which are preferentially or selectively attacked can also fail through increased thermal or electrical conductivity arising from severe metal infiltration and, in extreme cases, by complete penetration. Selective reaction occurs during the melting of phosphorus-deoxidized copper in alumino-silicate linings containing approximately 40% of alumina, and appears to be associated with the cuprous phosphate slag which results from the deoxidation of the copper. Free alumina in these linings, in the form of corundum, is not attacked but accumulates with silica in the deposit of eroded refractory.

If the reaction product has a melting point above the operational temperature, it is formed not only within the lining interstices in the zone of penetration, but may also tend to build-up on the metal/refractory interface. Otherwise, events in respect of such features as initial metal penetration and formation of an oxide barrier probably follow the course previously described. During the melting of copper-zinc alloys in alumino-silicate linings zinc aluminate, which has a melting point of 1950°C., is formed. This accumulates rapidly during the melting of brasses containing about 40% zinc, and most furnaces used for these alloys are withdrawn from service after melting 2000-3000 tons, because the cross-sectional area of the channel has by then diminished to an extent which renders further operation uneconomic. In melting brasses containing about 70% copper, the build-up of zinc aluminate is so slow that more than 20,000 tons have been melted with no significant change in channel dimensions. With copper-zinc alloys of higher copper content, such as gilding metals, channel enlargement is comparatively rapid, probably because of the increased erosion of the refractory at the higher operating temperatures involved.

Erosion is mainly responsible for channel enlargement where little or no reaction between refractory and melt occurs, as in the melting of phosphorus-deoxidized copper in siliceous linings. Although the effect is similar to that which occurs during the melting of phosphorus-deoxidized copper in alumino-silicate linings, inasmuch as it results in the accumulation of a deposit of eroded refractory in the lower

part of the channel, as shown in Figs. 20 and 21 (Plate XLV), erosion occurs more slowly, and lining lives of up to 2500 tons have been obtained, compared with a maximum of about 800 tons in alumino-silicate linings.

V.—CONCLUSION

No attempt has been made in this paper to trace chronologically or in detail the developments which have taken place in the use of refractories in low-frequency induction furnaces. What has been stated regarding constructional methods and factors affecting lining life is based on experience and experiment extending over more than thirty years, a period during which there have been a great many changes in dimensions, capacity, materials, techniques, and practices. In respect of lining life and economics of operation, the position is markedly different from that previously obtaining and, as a result of considerable and continuing improvement, this type of melting unit has become well established and is now a familiar and characteristic installation in modern non-ferrous plants. Although linings of high quality can be produced by the layer-ramming technique, the success of the method is largely dependent on the skill and experience of the operatives, and amongst further possible improvements are alternative, less exacting, methods of lining construction and the development of refractory materials for relatively high-melting-point alloys, such as the cupro-nickels and nickel silvers, which contain constituents that react rapidly with the types of refractories commonly used in these furnaces.

ACKNOWLEDGEMENT

The authors are grateful to many of their colleagues for helpful discussions in connection with the preparation of this paper.

REFERENCES

1. M. Cook and C. L. M. Cowley, *J. Inst. Metals*, 1952-53, **81**, 343.
2. H. W. Gillett and E. L. Mack, *U.S. Bur. Mines Bull.*, 1922, (202).
3. G. E. Taylor, *Elect. Rev.*, 1925, **97**, 327.
4. British Patent Application No. **34260/53**.
5. British Patent No. **692,498** (1953).

REPORT OF COUNCIL

FOR THE YEAR ENDED 31 DECEMBER 1954

THE year 1954 has for the Institute been the most active, and probably one of the most successful, in its history.

The most notable events of the year were the Joint Spring Meeting in London, at which members and ladies of the Société Française de Métallurgie were the guests of the Institute, and the Autumn Meeting, which was held in Switzerland by invitation of the Société Suisse des Constructeurs de Machines and the Association Suisse pour l'Essai des Matériaux.

The Joint Spring Meeting with the Société Française de Métallurgie was an unqualified success. There was a gratifyingly large attendance by members and ladies of the Société. The attendance—estimated to be of the order of 900—was probably the highest at any meeting of a British metallurgical society (there were times when about 550 persons were simultaneously present at scientific sessions), and the extensive programme of social functions and visits, including visits to provincial centres, was well supported. The Council feels that this meeting has not only provided an opportunity for the Institute to return in some measure the generous hospitality its members have received at two Autumn Meetings in Paris, but has also been the means of drawing more closely together those engaged in the science and practice of metallurgy in France and Great Britain. It is hoped that this will be the beginning of a series of such meetings, at intervals of about three years, at which the Institute will act as host to the members of European metallurgical societies.

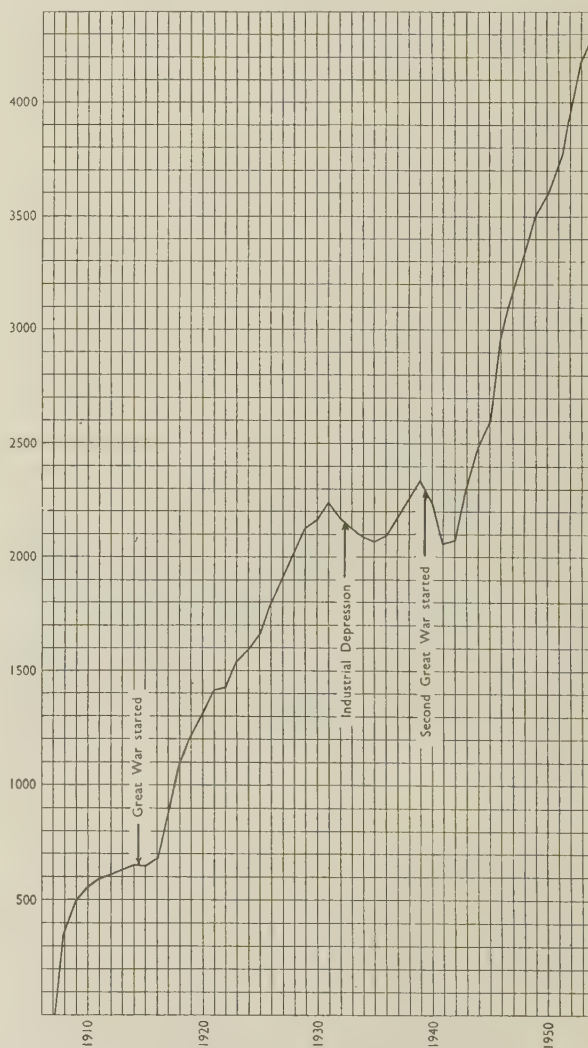
The Autumn Meeting in Switzerland was one of the most successful of its kind that the Institute has held, and the Council desires to place on record its deep sense of gratitude to the two Swiss associations which so generously entertained members and their ladies and to those industrial and research establishments which received members and also offered generous hospitality. The Council also wishes especially to thank the members of the Reception Committee and Mr. W. von Orelli for the care and thoroughness with which all the arrangements for the meeting were planned.

At the Spring Meeting, the Directors of Johnson, Matthey and Co., Ltd., presented to the Institute a Presidential Badge, incorporating the new Arms of the Institute, the expenses in connection with the grant of which the company also defrayed. The Council wishes to express to the Directors of the Company, on behalf of the members, its appreciation of this welcome and beautiful gift.

The volume of matter included in the *Bulletin*, *Journal*, and *Metallurgical Abstracts* has continued to increase; its publication has, in a large measure, been made possible by generous contributions received from the metallurgical, engineering, and chemical industries to the Industrial Donations Fund, for which the Council expresses its thanks.

FELLOW

During the year, Mr. H. S. TASKER, B.A. (Past-President), was elected a Fellow in recognition of his eminent services to the Institute.



Active Membership at 31 December 1908-1954.

MEMBERSHIP

The steady increase in the Institute's membership has been maintained, as is shown by the following table. There is, however, no doubt that the membership is capable of very considerable expansion throughout the world, and the Council hopes that members will during the coming year take every practicable step to interest persons within their own organizations and individual industries in the Institute's work and publications, in the hope that they may be introduced to membership.

The Secretary will be glad to send particulars of membership and specimen copies of the *Journal* to any potential members whose names are given to him.

At 31 December	1947	1948	1949	1950	1951	1952	1953	1954
Honorary Members . . .	9	9	11	11	11	11	11	11
Fellows . . .	7	6	9	10	8	8	9	9
Ordinary Members . . .	2491	2546	2685	2815	2941	3144	3368	3508
Junior Members	291	305	362	363	293
Associate Members . . .	17	19	18
Student Members . . .	655	746	783	452	462	423	417	457
Active List . . .	3179	3326	3506	3579	3727	3948	4168	4278
Suspense List . . .	36	55	67	97	124	95	131	157
TOTAL . . .	3215	3381	3573	3676	3851	4043	4299	4435

OBITUARY

The Council much regrets to record the death of Colonel Sir Paul Gueterbock, K.C.B., D.S.O., M.C., T.D., D.L., M.A., A.D.C., Past-President and Fellow.

It also records with regret the deaths of the following members: Mr. C. A. J. Heckford, Mr. N. F. S. Hubbard, Mr. J. E. Jenkins, Dr. S. Junghans, Mr. E. F. Law (an Original Member), Mr. E. F. MacTaggart, Mr. F. Mason (a former Member of Council), Mr. C. Nowell, Mr. F. Pechal, Mr. H.-E.-F. Rogez, Mr. James Steven (an Original Member), Mr. J. W. Stewart, Mr. J. E. Tolliday, Dr. A. Vambersky, Dr. C. M. Walter, Mr. H. B. Weeks (an Original Member and former Member of Council), and Mr. J. H. Wilson (an Original Member).

OFFICERS OF THE INSTITUTE

The following members were declared elected to fill honorary offices of the Institute with effect from the 1954 Annual General Meeting:

President:

S. F. DOREY, C.B.E., D.Sc., F.R.S., M.I.C.E.,
M.I.Mech.E., M.I.N.A.

Vice-Presidents:

MAURICE COOK, D.Sc., Ph.D., F.I.M.
L. B. PFEIL, O.B.E., D.Sc., A.R.S.M., F.R.S., F.I.M.
Major P. LITHERLAND TEED, A.R.S.M., F.R.Ae.S.,
M.I.M.M., F.I.M.

Ordinary Members of Council:

R. D. HAMER, B.Sc., F.I.M.
G. P. TINKER, M.Sc., F.I.M.

During the year, Mr. E. H. JONES resigned the Honorary Treasurership, owing to pressure of other duties, and Mr. J. C. COLQUHOUN, M.B.E., was elected to fill the vacancy.

In accordance with Article 42, the Council elected Dr. MAURICE COOK, F.I.M., as Senior Vice-President for the year 1954-55.

HONORARY CORRESPONDING MEMBERS TO THE COUNCIL

The Council wishes to express to all Honorary Corresponding Members its appreciation of their services and help during the past year.

Professor Dr. A. von Zeerleder resigned as Honorary Corresponding Member to the Council for Switzerland with effect from 31 December, and Dr. O. H. C. Messner has been appointed as his successor. The Council desires to place on record the Institute's indebtedness to Professor Dr. A. von Zeerleder, who had held the office of Honorary Corresponding Member since 1938, and had in that capacity rendered valuable services to the Institute.

The Honorary Corresponding Members to the Council were as follows: *Australia*: Professor H. K. Worner, D.Sc.; *Belgium*: H. P. A. Féron; *Canada*: G. S. Farnham, B.A., M.Sc., Ph.D., Professor F. A. Forward, B.A.Sc., and Professor G. Letendre, B.A., Ph.D.; *France*: Professor P. A. J. Chevenard and Jean Matter; *India*: N. P. Gandhi, M.A., B.Sc., A.R.S.M., D.I.C.; *Italy*: Leno Matteoli, Dott.chim.; *Netherlands*: M. Hamburger; *South Africa*: G. H. Stanley, D.Sc., A.R.S.M., and Professor L. Taverner, A.R.S.M., D.I.C.; *Spain*: Professor J. Orland, M.Sc., M.A., Ph.D., D.D.; *Sweden*: Professor Carl A. F. Benedicks, Fil.Dr., Dr.Ing.e.h., Dr.Tech.n.h.c., and Professor Axel Hultgren; *Switzerland*: O. H. C. Messner, Dipl.Ing., Dr.sc.techn., and Professor A. von Zeerleder, Dr.Ing., Dr.mont.h.c.; *United States of America*: Professor R. F. Mehl, Ph.D., Hon.Eng.D., Hon.Sc.D., Professor C. S. Smith, Sc.D., and Dr. R. A. Wilkins.

INSTITUTE OF METALS MEDAL

The Institute of Metals (Platinum) Medal for 1954 was awarded to Dr. Leslie Aitchison, M.Sc., in recognition of his services to metallurgy in industry, in education, and in public service.

W. H. A. ROBERTSON MEDAL AND PREMIUM

No award was made for the year 1953.

ROSENHAIN MEDAL

The Rosenhain Medal for 1954 was awarded to Professor A. H. Cottrell, B.Sc., Ph.D., Professor of Physical Metallurgy, University of Birmingham, in recognition of his outstanding contributions to knowledge in the field of physical metallurgy, with special reference to the deformation of metals.

CAPPER PASS AWARDS

The Adjudicating Committee made no awards during the year.

STUDENTS' ESSAY PRIZES

The Adjudicators awarded a prize of twenty guineas to Mr. Derek Hull, B.Sc., Student Member, for an essay on "The Characteristics of the Martensite Transformation". On the recommendation of the adjudicators, the essay was published in the July 1954 issue of the *Bulletin* (pp. 134-139).

PRESIDENTIAL BADGE AND GRANT OF ARMS

As mentioned on p. 306, at the 1954 Spring Meeting, Mr. Donald McDonald, on behalf of the Directors of Johnson, Matthey and Co., Ltd., presented to the Institute a Presidential Badge, incorporating the newly-granted Arms of the Institute, the costs connected with which the donors had also defrayed.

An illustration of the Presidential Badge is printed on p. 141 of the August 1954 issue of the *Bulletin*, and a full-page illustration of the Arms, in colour, will in due course be published in the form of a plate in the *Journal*.

PUBLICATIONS

During the financial year 1953-54, 77 papers and addresses were published in the *Journal*, comprising 784 pp. and 110 plates (compared with 689 pp. and 101 plates in 1952-53), and 720 pp. of *Metallurgical Abstracts* and annual indexes were printed (compared with 589 pp. in 1952-53). At the end of that financial year, however, there were still 41 MSS. in hand.

The publication of *Metallurgical Abstracts* has been brought further up to date, but—owing to difficulties in enlisting the services of a sufficient number of qualified abstractors to help keep pace with the growing volume of scientific and technical literature—the abstracting of a few journals fell in arrear. Steps are being undertaken to ensure that periodicals of the first importance to metallurgists shall receive priority in abstracting, so that prompt publication will be given to abstracts of papers of the highest importance. The Publication Committee appeals to the heads of University and industrial laboratories to encourage qualified members of their staffs and graduate students to assist the Institute with this abstracting work, for which the Institute has such a high reputation and which is of such vital importance to both science and industry.

The second (Subjects) volume of the General Index to Volumes 1-10 (1934-43) of *Metallurgical Abstracts* has been published. The MS. of the General Index to Volumes 11-20 (1944-53) has been completed, and the work of printing will be proceeded with as quickly as the staff position permits.

In the *Monograph and Report Series* a completely revised edition of No. 1: "The Structure of Metals and Alloys", by Dr. W. Hume-Rothery and Professor G. V. Raynor, has been published, as well as No. 16:

"The Control of Quality in the Production of Wrought Non-Ferrous Metals and Alloys. Part II.—The Control of Quality in Working Operations".

After careful consideration, and on the advice of a special Committee, representative of the membership of the Institute, under the Chairmanship of Dr. Ivor Jenkins, the Council has decided to proceed with the publication of a new quarterly periodical entitled *Metallurgical Reviews*. The object of the new journal will be to provide authoritative, critical and interpretative reviews of knowledge gained in various fields of interest to metallurgists, to satisfy as wide a circle of readers as possible. It is intended that *Metallurgical Reviews* shall cover the whole field of metallurgy except mining, the extraction of metals from their ores, and iron and steel works' practice, and that the contents shall be equally distributed as between industrial and theoretical topics.

The Council is satisfied that there is a widespread need for such a periodical, and trusts that it will be well supported by members.

GENERAL MEETINGS

On Wednesday, 6 January 1954, a General Meeting of the Institute was held in Birmingham, when there was an Informal Discussion, arranged by the Metallurgical Engineering Committee, on "Lubricants for Metal-Working Operations in the Non-Ferrous Metals Industry". There was a large attendance, and a valuable discussion, a report of which is given on pp. 100-104 of the April 1954 issue of the *Bulletin*.

The Spring Meeting was held in London, jointly with the Société Française de Métallurgie, from Monday, 26 April to Saturday, 1 May, with additional tours in provincial centres (Birmingham, Cambridge, Sheffield, and South Wales) from Sunday, 2 May to Tuesday, 4 May 1954, inclusive. There was a large attendance of members and ladies of the Société Française de Métallurgie, who were the Institute's guests on this occasion, and, in all, it is estimated that about 900 members and guests attended the meeting, which was a great success.

The Annual May Lecture was delivered at the Royal Institution, London, on Monday, 26 April 1954, by Professor L. F. Bates, D.Sc., Ph.D., F.R.S., whose subject was "The Domain Structure of Ferromagnetic Metals". The lecture was published in the *Journal*, 1953-54, Vol. 82, pp. 417-425.

During the year the Metal Physics Committee arranged two General Meetings in London, on the evenings of Thursday, 27 May, and Wednesday, 30 June, when lectures were delivered by Dr. W. Boas on "Lattice Defects and Energy Stored in Deformed Metals" and by Professor E. Orowan on "The Brittle Fracture of Metals: Some New Developments", respectively. There was a large attendance at each of these meetings.

The Autumn Meeting was held in Switzerland, from Monday, 6, to Tuesday, 14 September 1954, by invitation of the Société Suisse des Constructeurs de

Machines and the Association Suisse pour l'Essai des Matériaux. It was one of the most successful that the Institute has held. During the first week the meeting was located at Zürich, where scientific sessions were held and from whence a wide range of visits to works and laboratories took place. The Annual Autumn Lecture was delivered by Professor Dr. A. von Zeerleder on "Attempts to Improve Aluminium Reduction Since Héroult and Hall". From Zürich, members and ladies proceeded by special train to Montreux, from which a further series of visits was made on Monday and Tuesday, 13 and 14 September.

For the benefit of members who were unable to take part in the Autumn Meeting, a special General Meeting was held in London on Thursday and Friday, 25 and 26 November, at which there were discussions on a series of papers that had been published in the *Journal*.

LOCAL SECTIONS AND ASSOCIATED SOCIETIES

The six Local Sections of the Institute (Birmingham, London, Oxford, Scottish, Sheffield, and South Wales) had good programmes for their meetings during the winter session, which were well attended.

The arrangements made for meetings of the Sheffield Local Section to be held jointly with those of the Sheffield Society of Engineers and Metallurgists proved successful.

Members continued to enjoy the privilege of attending the meetings of the Associated Societies, viz. the Leeds Metallurgical Society, the Liverpool Metallurgical Society, the Manchester Metallurgical Society, and the North East Metallurgical Society.

A joint meeting was held at Bristol on 3 December 1954 with the Bristol Section of the Society of Chemical Industry and the Chemical Engineering Group, when Dr. A. R. Harding gave a lecture on "Thermochemistry of Alloys."

SPECIAL COMMITTEES

The Metal Physics Committee had 4 meetings during the year. It arranged two special General Meetings in London, to which reference has been made above, and is organizing a one-day Symposium in London in November 1955 on "The Mechanism of Phase Transformations in Metals".

The Metallurgical Engineering Committee met 3 times. It arranged an all-day Informal Discussion in Birmingham on 6 January on "Lubricants for Metal-Working Operations in the Non-Ferrous Metals Industry" and, in connection with the Spring Meeting, the second of a series of all-day Symposia on "The Control of Quality in the Production of Wrought Non-Ferrous Metals and Alloys. Part II.—The Control of Quality in Working Operations". During the year the Committee made plans for an Informal Discussion on "The Treatment of Swarfs, Sawings, and Residues in the Non-Ferrous Metal Industries", to be held in Birmingham on 16 February 1955; a discussion on "Refractories for Low-Frequency Induction Furnaces"; and for the final part of the

series of Symposia on the control of quality, the subject being "The Control of Quality in Heat-Treatment and Final Operations". The two latter discussions will be held in connection with the Spring Meeting 1955.

As a result of the report of a special Committee, under the Chairmanship of Dr. Ivor Jenkins, the Council has decided to publish a new journal, *Metallurgical Reviews*, to which reference is made on p. 308.

STAFF

The year 1954 has been marked by more than the usual activities of the Institute, the organization and arrangements for which have meant considerable additional work for the staff.

The Council desire to place on record their appreciation of the cheerful manner in which the Secretary and his staff have coped with the special demands made upon them and which has in no small measure contributed to the undoubted success of the meetings and social functions held during this year.

Mr. J. S. Cook joined the staff as an Editorial Assistant in place of Miss C. J. Arlidge, B.Sc.

JOINT ACTIVITIES

JOINT METALLURGICAL SOCIETIES' MEETING IN EUROPE

Certain of the national European metallurgical societies—the Iron and Steel Institute and the Institute of Metals (United Kingdom), the Société Française de Métallurgie (France), the Verein deutscher Eisenhüttenleute and the Deutsche Gesellschaft für Metallkunde (Germany), and the Jernkontoret (Sweden)—have jointly issued an invitation to the American Institute of Mining and Metallurgical Engineers and the American Society for Metals to hold a joint meeting in Europe from 1 to 18 June 1955. The invitation has been accepted.

His Royal Highness The Duke of Edinburgh has graciously consented to be Patron of the meeting in Great Britain.

Brief particulars of this meeting have already been published, and fuller details will be issued to all members in due course.

JOINT LIBRARY AND INFORMATION DEPARTMENT

The continued good use made of the services of the Library and Information Department is very gratifying; during the year 14,445 publications were borrowed, the corresponding figure for 1953 being 13,640. The Library acquired 268 new text-books in the same period (310 in 1953), and the Council desires to record its thanks to those donors to whom it is indebted for presentation copies of their works.

The use of the Library is one of the valuable privileges of membership of the Institute. The Reading Room is available to members to consult books and periodicals, including publications borrowed, on request through the Librarian, from other sources

such as the Science Library and the National Central Library, and those resident in the United Kingdom can borrow them for reading at home. Under certain conditions photographic copies of documents can be obtained for members, both in the United Kingdom and abroad, and during the year under review 128 photocopies and 99 microfilms were supplied (the corresponding figures for 1953 were 119 and 61).

The Information Department has been fully occupied with answering scientific and technical enquiries, but no record is kept of the number of cases dealt with. It must be stressed, however, that its function is not to give the type of advice that falls within the field of the metallurgical consultant.

In June 1954, Imperial Chemical Industries, Ltd., presented the Institute with a cheque for twenty guineas as a token of appreciation of the services rendered to the Company by the Joint Library; this donation will be spent on books or articles of use to the Library. The Council is very grateful for this gift.

JOINT COMMITTEE FOR NATIONAL CERTIFICATES IN METALLURGY

The total numbers of approved courses in operation during the session 1953-54 were: Senior Courses for the Ordinary National Certificate, 37; Contributory Centres, with Courses for the First Year or First and Second Years of the Senior Course, 6; Advanced Courses for the Higher National Certificate, 20.

The Joint Committee has recorded its gratitude to the Assessors for their valuable assistance in the operation of the scheme. Without this, its successful operation would not have been possible. (The Assessors have, in the year 1953-54, approved a total of 345 examination question papers and assessed the marks of 4234 examination scripts.)

Notes for guidance of Technical Colleges on the arrangement of Courses for National Certificates in Metallurgy are being prepared.

JOINT COMMITTEE ON METALLURGICAL EDUCATION

The Joint Committee on Metallurgical Education considered the question of further implementation of

the recommendations contained in the Report on "The Education and Training of Metallurgists".

A major recommendation in the Report is in process of being implemented as the result of the setting up of the Board of Metallurgical Studies and Examinations.

The implementing of other recommendations summarized in para. 58 of the Report is, in the Committee's opinion, a matter for consideration by Industry, the Training Committee of the British Iron and Steel Federation and the Non-Ferrous Industry, the Universities, and Technical Colleges.

MOND NICKEL FELLOWSHIPS COMMITTEE

The Mond Nickel Fellowships Committee made the following awards for 1954:

M. BROWNLEE (Dorman, Long and Co., Ltd., Redcar) to study British, Continental, and American hot-and cold-metal basic open-hearth steel-making, with particular reference to furnace design and construction and factors affecting ingot quality.

R. D. BUTLER (Imperial Chemical Industries, Ltd., Liverpool) to study mineral-dressing practice in Great Britain, on the Continent, and in the U.S.A. and Canada, with particular reference to the design, layout, and operation of small-scale mills.

F. B. PEACOCK (Dorman, Long and Co., Ltd., Middlesbrough) to study rolling-mill operation and maintenance, with particular reference to soaking pits, blooming mills, and the production of universal beams, structural sections, and rails.

A. M. SAGE (British Iron and Steel Research Association, London) to study the manufacture and fabrication of structural steels in the United Kingdom, Europe, the U.S.A., and Canada.

SIR GEORGE BEILBY MEMORIAL FUND

The Administrators of the Sir George Beilby Memorial Fund, representing the Institute of Metals, the Royal Institute of Chemistry, and the Society of Chemical Industry, made no awards from the Fund in respect of the year 1953.

APPENDIX I

LIST OF PAPERS PUBLISHED

The following is a complete list of the papers and lectures published by the Institute during the calendar year 1954

In the Journal

1513. The Constitution of Alloys of Aluminium, Copper, and Iron. By H. W. L. Phillips, M.A., F.R.I.C., F.Inst.P., F.I.M.
1514. The Oxidation of Titanium at High Temperatures in an Atmosphere of Pure Oxygen. By A. E. Jenkins, M.Eng.Sc.
1515. The Structure of Titanium-Silver Alloys in the Range 0-30 Atomic Per Cent. Silver. By H. W. Worner, M.Sc.
1516. The Metallographic Detection of Gamma Phase in Beta-Brass. By L. E. Samuels, B.Met.E.
1517. Mechanism of Creep Deformation in High-Purity Aluminium at High Temperatures. By Hsing C. Chang, M.S., Sc.D., and Nicholas J. Grant, B.S., Sc.D.
1518. Ageing Curves at 110° C. on Binary and Ternary Aluminium-Copper Alloys. By H. K. Hardy, M.Sc., Ph.D., A.R.S.M., A.I.M.
1519. Structural Ageing Characteristics of Binary Aluminium-Copper Alloys. By (Miss) J. M. Silcock, B.Sc., T. J. Heal, B.Sc., F.Inst.P., and H. K. Hardy, M.Sc., Ph.D., A.R.S.M., A.I.M.
1520. Changes of Damping Capacity in Quench-Ageing Aluminium-Rich Alloys. By K. M. Entwistle, M.Sc., Ph.D.
1521. Some Metallographic Observations of the Creep of Aluminium-Copper Alloys. By A. H. Sully, M.Sc., Ph.D., F.Inst.P., F.I.M., and H. K. Hardy, M.Sc., Ph.D., A.R.S.M., A.I.M.
1522. Problems of the Control of Dimension, Shape, and Finish in the Rolling of Sheet and Strip and in the Drawing of Wire. By Hugh Ford, D.Sc.(Eng.), Ph.D., Wh.Sch., and J. G. Wistreich, M.Sc.(Eng.), D.I.C.
1523. The Control of Quality in the Hot and Cold Rolling of Aluminium and Aluminium Alloys. By F. King, A.I.M., and A. N. Turner, B.Sc., Ph.D., A.R.S.M., A.I.M.
1524. The Control of Properties and Structure in the Hot and Cold Rolling of Copper and Copper-Base Alloys. By W. W. Kee, B.Sc., F.I.M.
1525. Some Factors Affecting the Quality of Extrusions. By Christopher Smith, F.I.M., and Norman Swindells, M.A., Ph.D., F.I.M.
1526. Statistical Control in Metal-Working Operations. By M. Whyte, B.Sc.
1527. The Forgeability, Creep Strength, and Ductility of Molybdenum and Some of its Alloys. By J. H. Rendall, B.Sc., A.R.S.M., A.I.M., S. T. M. Johnstone, B.Met.E., A.I.M., and W. E. Carrington.
1528. The Arc Melting of Metals and Its Application to the Casting of Molybdenum. By G. L. Hopkin, O.B.E., B.Sc., F.I.M., (Mrs.) J. E. Jones, B.Sc., D.R.T.C., A. R. Moss, and D. O. Pickman, B.A.
1529. The Pressure Welding of Molybdenum. By A. R. Moss.
1530. Factors Influencing Brittleness in Aluminium-Magnesium-Silicon Alloys. By I. R. Harris, D.R.T.C., A.I.M., and P. C. Varley, M.B.E., M.A., F.I.M.
1531. Techniques for the Investigation of Thermal Conditions in Continuous Casting. By D. M. Lewis, B.Sc., A.I.M.
1532. The Use of Autoradiography for Finding the Solidification Boundary in Continuously Cast Aluminium. By J. L. Putman, M.A.
1533. The Domain Structure of Ferromagnetic Metals. 44th May Lecture. By Professor L. F. Bates, Ph.D., D.Sc., F.R.S.
1534. The Influence of Extrusion Direction on the Corrosion and Stress-Corrosion of Aluminium-Copper-Magnesium Alloys. By E. A. G. Liddiard, M.A., F.I.M., and (Miss) Winifred A. Bell, B.A.
1535. A Redetermination and Interpretation of the Titanium-Rich Region of the Titanium-Chromium System. By (Mrs.) M. K. McQuillan, M.A.
1536. Resistivity Anomalies in the Nickel-Chromium System as Evidence of Ordering Reactions. By Rolf Nordheim, Chem.Eng., Sc.D., and Nicholas J. Grant, B.S., Sc.D.
1537. X-Ray Determination of the Alpha-Phase Boundary of the Copper-Indium Alloy System. By R. O. Jones, B.Sc., and Professor E. A. Owen, M.A., D.Sc.
1538. Some Further Observations on the Fatigue Process in Pure Aluminium. By P. J. E. Forsyth, A.I.M.
1539. The System Uranium-Mercury. By B. R. T. Frost, B.Sc., Ph.D.
1540. The Ternary Compound *E* in the System Aluminium-Chromium-Magnesium. By (Miss) K. Little, M.A., D.Phil.
1541. Staining of Clad Aluminium Alloy Sheets During Salt-Bath Heat-Treatment. By E. C. Williams, M.Sc., A.Inst.P., and H. J. G. Challis, F.R.I.C., A.I.M.
1542. The Constitution of Gold-Molybdenum Alloys, with Particular Reference to the Solubility of Molybdenum in Gold. By G. A. Geach, M.Sc., Ph.D., F.I.M., and D. Summers-Smith, B.Sc., Ph.D., A.R.T.C.
1543. Metallographic Observations on Cell Formation and Development in Aluminium. By J. W. Kelly, M.Sc., and R. C. Giffins, B.Sc., A.I.M.
1544. Some Observations on the Deformation of Zinc at High Temperatures. By R. W. Cahn, Ph.D., (Miss) I. J. Bear, A.M.T.C., and R. L. Bell, B.Sc.
1545. Methods for Determining the Liquidus Points of Titanium-Rich Alloys. By W. Hume-Rothery, O.B.E., F.R.S., and D. M. Poole, B.Sc., M.Sc.
1546. Isothermal Transformations of Hypo-Eutectoid Aluminium Bronzes. By R. Haynes, B.Met., Ph.D., A.I.M.
1547. Metals and Marine Engineering. Presidential Address. By S. F. Dorey, C.B.E., D.Sc., F.R.S.
1548. Note on the Constitution of the Titanium-Gold System in the Region 0-6 Atomic Per Cent. Gold. By (Mrs.) M. K. McQuillan, M.A.
1549. Grain-Refining Additions for Cast Copper Alloys. By A. Cibula, M.A., A.I.M.
1550. Exploratory Creep Tests on Metals of High Melting Point. By N. P. Allen, D.Sc., M.Met., F.I.M., and W. E. Carrington.
1551. The Constitution of the Titanium-Rich Alloys of Titanium, Iron, and Oxygen. By N. P. Allen, D.Sc., M.Met., F.I.M., T. H. Schofield, M.Sc., F.I.M., and (Mrs.) B. Mellish, B.Sc.
1552. The Constitution of the Copper-Rich Copper-Zinc-Gallium Alloys. By T. B. Massalski, B.Sc., and Professor G. V. Raynor, M.A., D.Sc.
1553. A Study of Preferred Orientation in Extruded, Drawn, and Annealed Copper. By Professor Paul G. Bastien, Dr.ès Sci., and Dr. J. Pokorný.
1554. The Cleavage Fracture of Pure Polycrystalline Zinc in Tension. By G. W. Greenwood, B.Sc., Ph.D., and Professor A. G. Quarrell, D.Sc., Ph.D., A.R.C.S.
1555. Preferred Orientation in Rolled Uranium Sheet. J. Adam, B.Sc., Ph.D., A.Inst.P., and J. Stephenson, B.Met., A.I.M.
1556. The Constitution of the System Silver-Lithium. By W. R. Freeth, Ph.D., B.Sc., and Professor G. V. Raynor, M.A., D.Sc.
1557. The Systems Magnesium-Lithium and Magnesium-Lithium-Silver. By W. E. Freeth, Ph.D., B.Sc., and Professor G. V. Raynor, M.A., D.Sc.

1558. Grain-Boundary Movement, Slip, and Fragmentation During Creep of Aluminium-Copper, Aluminium-Magnesium, and Aluminium-Zinc Alloys. By D. McLean, D.Sc., and M. H. Farmer, B.Sc., A.I.M., F.R.M.S.
1559. Fatigue Phenomena in High-Strength Aluminium Alloys. By R. F. Hanstock, Ph.D., F.Inst.P.
1560. The Ageing Characteristics of Some Ternary Aluminium-Copper-Magnesium Alloys with Copper: Magnesium Weight Ratios of 7:1 and 2:2:1. By H. K. Hardy, M.Sc., Ph.D., A.R.S.M., A.I.M.
1561. A High-Resolution Evaporated-Carbon Replica Technique for the Electron Microscope. By D. E. Bradley.
1562. The Formation and Removal of Twins in Titanium During Deformation. By A. T. Churchman, Ph.D., B.Sc., A.I.M.
1563. Influence of Cold Deformation on the Young's Modulus of Some Non-Ferrous Metals. By Maurice Cook, D.Sc., Ph.D., F.I.M., T. Ll. Richards, B.Sc., Ph.D., F.I.M., and G. F. Bidmead, B.Sc., A.I.M., A.C.T.(Birm.).
1564. The Solid Solution of Cadmium in Zinc. By J. R. Brown, B.A.
1565. Growth Twins in Crystals of Low Co-Ordination Number. By E. Billig, D.Sc.Tech., M.I.E.E.
1566. Twinning and Untwinning in Polycrystalline Magnesium. By R. L. Woolley, M.A., Ph.D., A.Inst.P.
1567. The Viscosity of Copper and Some Binary Copper Alloys. By Professor W. R. D. Jones, D.Sc., and W. L. Bartlett, B.Sc., Ph.D.
1568. The Bainitic Transformation of the Beta Phase in Copper-Zinc Alloys. By R. D. Garwood, M.Sc.
1569. The Creep and Fatigue Properties of Some Wrought Complex Aluminium Bronzes. By J. McKeown, D.Sc., F.I.M., D. N. Mends, B.Sc., A.I.M., E. S. Bale, L.I.M., and A. D. Michael, B.Sc., A.I.M.
1570. The Effect of Strain Rate and Temperature on the Resistance of Aluminium, Copper, and Steel to Compression. By J. F. Alder, M.A., Ph.D., Grad.I.C.E., and V. A. Phillips, A.R.S.M., B.Sc., D.Eng., A.I.M.
1571. The Selective Oxidation of Nickel-Chromium Alloys at High Temperatures. By J. Moreau, Ing.Dr., and Professor J. Bénard, Dr.ès Sci.
1572. Diffusion of Nitrogen and Oxygen in Titanium. By R. J. Wasilewski, B.A., and G. L. Kehl.
1573. Isothermal Transformations of Eutectoid Aluminium Bronzes. By R. Haynes, B.Met., Ph.D., A.I.M.
1574. Strain-Ageing in 70:30 Brass. By B. B. Hundy, Ph.D., B.Sc., A.I.M.
1575. Corrosion-Fatigue Properties of an Aluminium-Magnesium-Silicon Alloy in the Unprotected, Anodized, and Painted Conditions. By N. P. Inglis, Ph.D., M.Eng., M.I.Mech.E., F.I.M., and E. C. Larke, A.M.I.Mech.E., A.I.M.
1576. The Electrodeposition and Refining of High-Grade Chromium. By H. T. Greenaway, B.Met.E.
1577. The Fabrication of Chromium and Some Dilute Chromium-Base Alloys. By F. Henderson, S. T. Quaass, B.Met.E., M.Eng.Sc., A.I.M., and H. L. Wain, B.Met.E., Ph.D.
1578. A Study of the Room-Temperature Ductility of Chromium. By H. L. Wain, B.Met.E., Ph.D., F. Henderson, and S. T. M. Johnstone, B.Met.E., A.I.M. With an Appendix on Analytical Methods Used for the Determination of Nitrogen and Oxygen in Chromium. By E. J. Lumley.
1579. The Surface Tension of Sodium. By J. W. Taylor, Ph.D., B.Sc., A.R.T.C.

In the Bulletin

- B6. Lubricants for Metal-Working Operations in the Non-Ferrous Metals Industry. (Report of an Informal Discussion.)
- B7. Production and Properties of High-Purity Nickel Powder. By Professor F. A. Forward, B.A.Sc.
- B8. The Characteristics of the Martensite Transformation. By D. Hull, B.Sc. (Student's Prize Essay.)
- B9. A Review of Developments in the Melting, Refining, and Casting of Copper. By H. J. Miller, M.Sc., F.I.M.
- B10. Some Techniques of Constitutional Metallurgy (Birmingham Local Section Symposium):
- The Examination of Surface Topography by Interferometric Methods. By W. D. Biggs, B.Sc., A.I.M.
- The Hot-Stage Microscope and its Use with the Ciné-Camera. By S. G. Glover, B.Sc.
- Examination of Metallic Surfaces by Electron-Diffraction Methods. By E. C. Williams, M.Sc., A.Inst.P.
- Electron-Optical Methods in Constitutional Metallurgy. By J. W. Menter, M.A., Ph.D., A.Inst.P.
- Automatic Recording of Dilatometer Measurements. By F. G. Haynes, M.Eng.
- Continuous Cooling Transformations in Steels. By G. Mayer, B.Sc.

APPENDIX II

CONTRIBUTIONS TO THE INDUSTRIAL DONATIONS FUND IN, OR FOR, THE FINANCIAL YEAR ENDED 30 JUNE 1954

Donor	Gross, after Recovery of Tax by the Institute		Donor	Gross, after Recovery of Tax by the Institute	
	£	s. d.		£	s. d.
*Enfield Rolling Mills, Ltd. (incl. Enfield Copper Refining Co., Ltd.; Enfield Rolling Mills (Aluminium), Ltd.; Holloway Metal Roofs, Ltd.; and London Zinc Mills, Ltd.)	500	0 0	Rubery, Owen and Co., Ltd.	75	6 6
*Mond Nickel Co., Ltd., The (incl. Birlec, Ltd.; Henry Wiggin and Co., Ltd., and associated companies in the United States and Canada)	500	0 0	Mallory Metallurgical Products, Ltd.	52	10 0
*Consolidated Zinc Corporation, Ltd., The (incl. The Broken Hill Corporation, Ltd.; Imperial Smelting Corporation, Ltd.; The National Smelting Co., Ltd.; New Broken Hill Consolidated, Ltd.; Northern Smelting and Chemical Co., Ltd.; Sulphide Corporation Ltd.; and The Zinc Corporation, Ltd.)	454	10 11	Pyrotenax, Ltd.	52	10 0
*Goodlass Wall and Lead Industries, Ltd.: Associated Lead Industries, Ltd.	£181	16 4	*Associated Electrical Industries, Ltd., on behalf of the A.E.I. Group of Companies	50	0 0
Fry's Metal Foundries, Ltd. (incl. Antifriction Bearing Co., Ltd., The; Atlas Metal and Alloys, Ltd.; and The Eyre Smelting Co., Ltd.)	£90	18 2	Austin Motor Co., Ltd.	50	0 0
*Mufulira Copper Mines, Ltd.	272	14 6	Birmingham Battery and Metal Co., Ltd., The	50	0 0
*Roan Antelope Copper Mines, Ltd.	272	14 6	*Dale (John), Ltd.	50	0 0
*Imperial Chemical Industries, Ltd., and its subsidiary companies	†250	0 0	G.K.N. Group	50	0 0
Aluminium Laboratories, Ltd. (incl. Aluminium Union, Ltd.; Northern Aluminium Co., Ltd.; and Stand, Ltd.)	200	0 0	Lucas (Joseph), Ltd. (incl. Rotax, Ltd.)	50	0 0
General Motors, Ltd. (incl. A.C. Sphinx Spark Plug Co., Ltd.; Delco-Remy-Hyatt, Ltd.; and Frigidaire, Ltd.)	200	0 0	*Murex, Ltd. (incl. Murex Welding Processes, Ltd.)	50	0 0
Tube Investments, Ltd. (incl. The Chesterfield Tube Co., Ltd.; Mersey Cable Works, Ltd.; Reynolds Light Alloys, Ltd.; Reynolds Rolling Mills, Ltd.; Simplex Electric Co., Ltd.; South Wales Aluminium Co., Ltd.; and T.I. Aluminium, Ltd.)	200	0 0	Rolls-Royce, Ltd.	50	0 0
*British Aluminium Co., Ltd., The (incl. Aluminium Corporation, Ltd.; William Mills, Ltd.; and North British Aluminium Co., Ltd.)	181	16 4	*Tennant (C.), Sons and Co., Ltd.	†50	0 0
*McKeehn Brothers, Ltd.	181	16 4	*Brown (David) and Sons (Huddersfield), Ltd.	†47	14 6
*Magnesium Elektron, Ltd. (incl. F. A. Hughes and Co., Ltd.)	181	16 4	*Morgan Crucible Co., Ltd.	47	14 6
*Metallo-Chemical Refining Co., Ltd.	181	16 4	*Simon-Carves, Ltd.	47	14 6
Nchanga Consolidated Copper Mines, Ltd.	150	0 0	*Hopkinsons, Ltd.	47	5 3
Rhodesia Broken Hill Development Co., Ltd., The	150	0 0	*A.P.V. Co., Ltd.	45	9 1
Rhokana Corporation, Ltd.	150	0 0	*Birmetals, Ltd.	45	9 1
Vickers-Armstrongs, Ltd., and Vickers, Ltd. (incl. A.B.C. Motors, Ltd.; Robert Boby, Ltd.; Cooke, Troughton and Simms, Ltd.; Ioco, Ltd.; George Mann and Co., Ltd.; Palmers Hebburn Co., Ltd.; G. J. Worssam and Son, Ltd.; and Powers-Samas Accounting Machines, Ltd.)	105	0 0	*Birmingham Aluminium Casting (1903) Co., Ltd.	45	9 1
Copper Pass and Son, Ltd. (incl. George Pizey and Co., Ltd.; The Tyne Solder Co., and Victor G. Stevens, Ltd.)	100	0 0	*Bristol Aeroplane Co., Ltd., The	45	9 1
Colvilles, Ltd.	100	0 0	*British Metal Corporation, Ltd., The	45	9 1
Johnson (Richard) and Nephew, Ltd.	100	0 0	*Chloride Electrical Storage Co., Ltd., The	45	9 1
Johnson, Matthey and Co., Ltd.	100	0 0	*Essex Aero, Ltd.	45	9 1
*Manganese Bronze and Brass Co., Ltd., The	†95	9 1	*London and Scandinavian Metallurgical Co., Ltd.	45	9 1
*Consolidated Tin Smelters, Ltd. (incl. The Cornish Tin Smelting Co., Ltd.; Eastern Smelting Co., Ltd.; The Penpoll Tin Smelting Co., Ltd.; and Williams, Harvey and Co., Ltd.)	90	18 2	*Rotol, Ltd.	45	9 1
*Enthoven (H. J.) and Sons, Ltd.	90	18 2	*Star Aluminium Co., Ltd. (incl. Anglo-Swiss Aluminium Co., Ltd.)	45	9 1
*High Duty Alloys, Ltd.	90	18 2	*Sterling Metals, Ltd.	45	9 1
*Stone (J.) and Co. (Charlton), Ltd.	†90	18 2	*Telegraph Construction and Maintenance Co., Ltd., The (incl. Submarine Cables, Ltd.)	†45	9 1
*Venesta, Ltd.	90	18 2	*Wolverhampton Metal Co., Ltd., The (incl. James Bridge Copper Works, Ltd.)	45	9 1
*Whiley (Geo. M.), Ltd.	90	18 2	Wednesbury Tube Co., Ltd., The	42	0 0
			*Hughes-Johnson Stampings, Ltd., The	38	3 8
			*Light Metal Forgings, Ltd.	38	3 8
			*Ferranti, Ltd.	36	8 0
			*Gibbons Brothers, Ltd. (incl. The Thermic Equipment and Engineering Co., Ltd.)	36	8 0
			*Parkinson Stove Co., Ltd., The	†36	7 3
			Aluminum Company of America (\$100)	35	7 7
			*British Tin Investment Corporation, Ltd.	28	12 9
			*Derby and Co., Ltd.	28	12 9
			*London Electric Wire Company and Smiths, Ltd., The (incl. Liverpool Electric Cable Co., Ltd.)	†28	12 9
			*Barker and Allen, Ltd.	27	5 5
			*Bolton (Thomas) and Sons, Ltd.	27	5 5
			*British Lead Mills, Ltd.	27	5 5
			English Electric Co., Ltd., The (incl. D. Napier and Son, Ltd.)	26	5 0
			Head, Wrightson and Co., Ltd.	26	5 0
			Arkinstall Brothers, Ltd.	25	0 0
			Braby (Frederick) and Co., Ltd.	25	0 0
			British Timken, Ltd. (incl. Fischer Bearings Co., Ltd.)	25	0 0
			British United Shoe Machinery Co., Ltd., The	25	0 0
			Davy and United Engineering Co., Ltd.	25	0 0
			Fairey Aviation Co., Ltd., The	25	0 0
			Gardner (Henry) and Co., Ltd.	25	0 0
			*Holroyd (John) and Co., Ltd.	25	0 0
			Messina Transvaal Development Co., Ltd., The	25	0 0
			Plessey Co., Ltd., The	25	0 0
			Pressed Steel Co., Ltd.	25	0 0
			Thompson (John) (Wolverhampton), Ltd.	25	0 0
			Metal Box Co., Ltd., The	22	1 0
			Bull's Metal and Marine Co., Ltd.	21	0 0

Donor	Gross, after Recovery of Tax by the Institute			Donor	Gross, after Recovery of Tax by the Institute		
	£	s.	d.		£	s.	d.
Delta Metal Co., Ltd., The (incl. Heaton and Dugard, Ltd.)	21	0	0	Vauxhall Motors, Ltd.	10	10	0
Fulmer Research Institute, Ltd.	21	0	0	Allen (W. H.), Sons and Co., Ltd.	10	0	0
Leigh and Sillavan, Ltd.	21	0	0	Electric Furnace Co., Ltd. (incl. Electro-Chemical Engineering Co., Ltd.)	10	0	0
Monotype Corporation, Ltd., The	21	0	0	Electric Resistance Furnace Co., Ltd.	10	0	0
Philips Electrical, Ltd.	21	0	0	Highton and Son, Ltd.	10	0	0
Brightside Foundry and Engineering Co., Ltd., The	20	0	0	Metro-Cutanit, Ltd.	10	0	0
Deloro Stellite, Ltd.	20	0	0	Rothschild (N. M.) and Sons	10	0	0
*International Alloys, Ltd.	20	0	0	*Winfields Rolling Mills, Ltd.	10	0	0
Hall and Pickles, Ltd.	20	0	0	*Central Marine Engine Works (William Gray and Co., Ltd.)	9	11	0
Hard Metal Tools, Ltd.	20	0	0	*Corfield-Sigg, Ltd.	9	11	0
Park Gate Iron and Steel Co., Ltd., The	20	0	0	*Harland Engineering Co., Ltd., The	9	11	0
Renfrew Foundries, Ltd.	20	0	0	*Wild-Barfield Electric Furnaces, Ltd.	9	11	0
Sheffield Smelting Co., Ltd.	20	0	0	*Bound Brook Bearings (G.B.), Ltd.	9	1	0
Société Anonyme pour l'Industrie de l'Aluminium (Lausanne, Switzerland)	20	0	0	*Hoyt Metal Company of Great Britain, Ltd., The	9	1	0
Wickman, Ltd.	20	0	0	*Hunt and Mitton, Ltd.	9	1	0
*Allen (Edgar) and Co., Ltd.	19	1	10	*Jenkinson (W. G.), Ltd.	9	1	0
*British Tin Smelting Co., Ltd., The	19	1	10	*Shaw, Son and Greenhalgh, Ltd.	9	1	0
*General Electric Co., Ltd., The	19	1	10	*Stein (John G.) and Co., Ltd.	9	1	0
*Phosphor Bronze Co., Ltd., The	19	1	10	*Betts and Co., Ltd.	7	12	9
*Saunders-Roe, Ltd.	19	1	10	*Glenfield and Kennedy, Ltd.	7	12	9
*Chase Non-Ferrous Metal Co., Ltd.	18	3	7	United Wire Works (Birmingham), Ltd.	6	6	0
*Curran (Edward) Engineering, Ltd.	18	3	7	Acton Bolt, Ltd.	5	5	0
*Rollet (H.) and Co., Ltd.	18	3	7	Bawn (W. B.) and Co., Ltd.	5	5	0
*Wolverhampton Die-Casting Co., Ltd., The	18	3	7	Blackwells Metallurgical Works, Ltd.	5	5	0
Marconi's Wireless Telegraph Co., Ltd.	15	15	0	Dennison Watch Case Co., Ltd.	5	5	0
Perry Barr Metal Co., Ltd.	15	0	0	Easdale (R. M.) and Co.	5	5	0
*Scottish Non-Ferrous Tube Industries, Ltd.	15	0	0	Electro-Alloys, Ltd.	5	5	0
*Loewy Engineering Co., Ltd., The	13	12	9	Electroflo Meters Co., Ltd.	5	5	0
Brotherhood (Peter), Ltd.	12	12	0	Headley, Birch and Co., Ltd.	5	5	0
Bellis and Morecom, Ltd. (incl. W. Sisson and Co., Ltd.)	10	10	0	Langley Alloys, Ltd.	5	5	0
Carborundum Co., Ltd., The	10	10	0	Lead Wool Co., Ltd., The	5	5	0
Clifford (Charles) and Son, Ltd.	10	10	0	Miles (John) and Partners (London), Ltd.	5	5	0
Copper and Alloys, Ltd.	10	10	0	Ratcliffs (Great Bridge), Ltd.	5	5	0
Elliott Brothers (London), Ltd.	10	10	0	Rigby (John) and Sons, Ltd.	5	5	0
Foundry Services, Ltd.	10	10	0	Wilkinson (John) and Sons (Saltley), Ltd.	5	5	0
Fry's Diecastings, Ltd.	10	10	0	Cambridge Instrument Co., Ltd.	5	0	0
G. W. B. Electric Furnaces, Ltd.	10	10	0	Blakeborough (J.) and Sons, Ltd.	4	4	0
Glynn Brothers, Ltd.	10	10	0	Kincaid (John G.) and Co., Ltd.	4	4	0
Harrison (Birmingham), Ltd.	10	10	0	*Acorn Anodising Co., Ltd.	†3	12	9
Hoover, Ltd.	10	10	0	*Platt Metals, Ltd.	3	12	9
Incandescent Heat Co., Ltd., The (incl. Controlled Heat and Air, Ltd.; Metal Porcelains, Ltd.; Metaelectric Furnaces, Ltd.; and Selas Gas and Engineering Co., Ltd.)	10	10	0	Metal Information Bureau, Ltd.	3	3	0
*Maudslay Motor Co., Ltd., The	10	10	0	Mining and Chemical Products, Ltd.	3	3	0
Newey and Tayler, Ltd. (incl. Newey Brothers, Ltd., and D. F. Tayler and Co., Ltd.)	10	10	0	Tungum Sales Co., Ltd.	3	3	0
*North Thames Gas Board	10	10	0	Walterisation Co., Ltd., The	3	3	0
*North Thames Gas Board for 1952-53	†10	10	0	Beryllium and Copper Alloys, Ltd.	2	2	0
Rover Co., Ltd., The	10	10	0	Carobronze, Ltd.	2	2	0
Strebor Diecasting Co., Ltd.	10	10	0	Follsain-Wycliffe Foundries, Ltd.	2	2	0
				Gascoignes Non-Ferrous Foundries, Ltd.	2	2	0
				Premier Cooler and Engineering Co., Ltd., The	2	2	0
				Sheffield Testing Works, Ltd., The	2	2	0
				Metal Supplies, Ltd.	2	0	0
				Jenks (E. P.), Ltd.	1	1	0

* Annual Donation, Under Covenant, for Not Less than 7 Years.

† Includes tax recoverable, but not actually recovered in the financial year 1953-54.

‡ Amounts received after the end of the financial year 1952-53 and not included in the list of donations for that year.

APPENDIX III

COMMITTEES

The main committees of the Institute which have served during the year were constituted as follows at 31 December 1954 :

FINANCE AND GENERAL PURPOSES COMMITTEE

JONES, Mr. E. H. (<i>Chairman</i>).	<i>Ex-officio :</i>
BAILEY, Mr. G. L.	DOREY, Dr. S. F. (<i>President</i>).
GRIMSTON, The Hon. John.	COOK, Dr. Maurice (<i>Senior Vice-President</i>).
MURPHY, Professor A. J.	COLQUHOUN, Mr. J. C. (<i>Honorary Treasurer</i>).
RAMSAY, Dr. A. G.	SMITH, Mr. C. (<i>Chairman, Publication Committee</i>).
SMITHELLS, Dr. C. J.	
TEED, Major P. L.	
THOMPSON, Professor F. C.	

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BOLTON, Mr. E. A.	SINGER, Dr. A. R. E.
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BOWMAN, Mr. W. H.	WILKINSON, Mr. R. G.
CAMPBELL, Mr. D. F.	
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LAKE, Mr. N. C.	SMITH, Mr. C. (<i>Chairman, Publication Committee</i>).
MILLER, Mr. H. J.	

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ASHTON, Mr. A. B.	MADDOCKS, Dr. W. R. (<i>Chairman, Sheffield Local Section</i>).
GARSDIE, Dr. J. E.	MACDOUGALL, Mr. A. J. (<i>Honorary Secretary, Sheffield Local Section</i>).
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SMITH, Mr. S. S. (<i>Chairman, Birmingham Local Section</i>).	CUNNIFFE, Mr. P. W. A. (<i>Honorary Secretary, South Wales Local Section</i>).
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CHASTON, Dr. J. C. (<i>Chairman, London Local Section</i>).	<i>Ex-officio :</i>
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PARKER, Dr. R. T. (<i>Chairman, Oxford Local Section</i>).	COOK, Dr. Maurice (<i>Senior Vice-President</i>).
SMITH, Mr. O. R. (<i>Honorary Secretary, Oxford Local Section</i>).	COLQUHOUN, Mr. J. C. (<i>Honorary Treasurer</i>).
MACDONALD, Mr. G. (<i>Chairman, Scottish Local Section</i>).	

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BAKER, Dr. W. A.	<i>Ex-officio :</i>
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FORD, Professor H.	JONES, Mr. E. H. (<i>Chairman, Finance and General Purposes Committee</i>).
GADD, Mr. E. R.	COLQUHOUN, Mr. J. C. (<i>Honorary Treasurer</i>).
HOAR, Dr. T. P.	
RAYNOR, Professor G. V.	
SALTER, Mr. J.	
SCHUEER, Dr. E.	
SMITH, Mr. Christopher.	
SMITH, Mr. S. S.	
and	
Dr. L. NORTHCOTT (representing the Institution of Metallurgists).	

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BAILEY, Mr. R. W.	DOREY, Dr. S. F. (<i>President</i>).
BAKER, Dr. W. A.	JONES, Mr. E. H. (<i>Chairman, Finance and General Purposes Committee</i>).
FINNISTON, Dr. H. M.	COLQUHOUN, Mr. J. C. (<i>Honorary Treasurer</i>).
FORD, Professor H.	RAYNOR, Professor G. V. (<i>Chairman, Metal Physics Committee</i>).
HUDSON, Mr. F.	THOMAS, Mr. W. J. (<i>Chairman, Metallurgical Engineering Committee</i>).
INGLIS, Dr. N. P.	
JENKINS, Dr. Ivor.	
PARKER, Dr. R. T.	
PFEIL, Dr. L. B. (representing Local Sections Committee).	
PHILLIPS, Mr. H. W. L.	
POWELL, Mr. A. R.	
SHOWELL, Mr. D. W. D.	

The constitution of certain Committees was fixed by standing orders of the Council, as follows :

METAL PHYSICS COMMITTEE

RAYNOR, Professor G. V. (<i>Chairman</i>).	RICHARDS, Dr. T. Ll.
AXON, Dr. H. J.	RICHARDSON, Dr. F. D.
BAILEY, Dr. G. L. J.	SULLY, Dr. A. H.
CHRISTIAN, Dr. J. W.	WAKEMAN, Dr. D. W.
FINNISTON, Dr. H. M.	
FORSYTH, Mr. P. J. E.	
FRANK, Professor F. C.	
GEACH, Dr. G. A.	
HANSTOCK, Dr. R. F.	
KING, Mr. R.	
NUTTING, Dr. J.	<i>Ex-officio :</i>
OLIVER, Mr. D. A. (representing the Iron and Steel Institute and the British Iron and Steel Research Association).	DOREY, Dr. S. F. (<i>President</i>).
	SMITH, Mr. C. (<i>Chairman, Publication Committee</i>).

MEDAL COMMITTEE

PRESIDENT (<i>Chairman</i>).	lists who are, or have been, members of the Council (to be selected by the President), with power to the President to co-opt not more than two other persons.
SENIOR VICE-PRESIDENT.	
and	
Not more than four Institute of Metals (Platinum) Medal	

NOMINATIONS COMMITTEE

PRESIDENT (<i>Chairman</i>).
TWO IMMEDIATE PAST-PRESIDENTS.
SENIOR VICE-PRESIDENT.

STAFF COMMITTEE

CHAIRMAN, FINANCE AND GENERAL PURPOSES COMMITTEE.
HONORARY TREASURER.

REPORT OF THE HONORARY TREASURER

(Mr. E. H. JONES, A.R.I.C., M.I.M.M., F.I.M.)

FOR THE FINANCIAL YEAR ENDED 30 JUNE 1954

As will be seen from the Report of Council, the year has again been a very active one, and this is reflected in increases in both income and expenditure. The main items of increase in income are members' subscriptions £594 and advertisement revenue £900.

Production and despatch costs of the *Journal* and *Metallurgical Abstracts* increased by £2327 to £22,728, and when appropriate overheads are added, the total cost of the *Journal* for the year was £34,547. Some 28% of this, £9638, was recovered as advertisement revenue, while sales of the *Journal* realized £7306. Allowing for postages recovered, this means that copies cost just over £4 per annum for each member receiving them as part of the service of the Institute.

Our estimate of the number of papers likely to be submitted to, and accepted by, the Publication Committee last year was much too low, and the indications are that it may increase even further. The Institute thus faces a serious financial problem. The Special Publications are priced to members and non-members to pay their way, and it would be impossible to make any substantial saving on general administration. Therefore the expenditure on the *Journal* must be adjusted to maintain the Institute in a solvent condition. The Publication Committee selects on merit only, and for the Council to instruct it to select on a basis of available space would be a reversal of policy that might, in the long run, do considerable harm.

It is hoped, therefore, that Industry will continue to subscribe to the Industrial Donations Fund at around the present level, but we cannot yet be sure of this. The officers and Council are giving very careful thought to the solution of this problem. It will be seen that the excess of expenditure over normal income for the year rose from £5076 to £6639, owing, as previously stated, to an increase in publication costs. This is more than covered by the year's net income from the Industrial Donations Fund (£7860), but that

is not to be regarded as permanent income. It does, however, give the Institute time to take steps to reverse the trend. The sum of £1561 spent in entertaining the members of the Société Française de Métallurgie is an item that does not recur each year, but, with the approaching end of the Institute's lease of offices at 4 Grosvenor Gardens, provision will have to be made for an increase in rent of office accommodation of around £1000 per annum.

In the balance sheet, the deficiency in the Income and Expenditure account has been transferred to the Accumulated Fund from the Industrial Donations Fund. The Mond Nickel Fellowships Fund is reduced by £4634, almost all of which represented grants to Fellows. The Fund's income has now ceased, and this reduction will continue as grants are awarded in future years.

The cost of publication has been stressed in this report, but it is a problem common to most scientific and technical societies. Thanks to the generous help of the Industry, the finances of the Institute are relatively very sound, but Industry is being asked to support more and more worthy causes, and the Institute must take every possible step to keep help from this source to an absolute minimum.

The Institute itself has not been unsuccessful in increasing its normal income since the war. In this connection, members may be interested to know that the normal income from members' subscriptions, investments, sales of publications, and advertisements has increased by 170.86 per cent. since 1945-46, and that since the appeal was made to Industry for financial support in 1950 the normal income (that is, excluding the industrial subscriptions) has increased by 43.08 per cent.

This growth in income indicates the increasing appreciation throughout the world of the valuable services—especially in the field of publications—which the Institute is providing for metallurgical science and industry.

THE INSTITUTE OF METALS

[illegible]

REPORT TO THE MEMBERS OF THE INSTITUTE OF METALS

We have audited the above Balance Sheet dated 30 June 1954, and the annexed Income and Expenditure Account for the year ended 30 June 1954, and report that we have obtained all the information and explanations which to the best of our knowledge and belief were necessary for the purposes of our audit.

The above-mentioned Balance Sheet and annexed Income and Expenditure Account are in agreement with the Books of Account. In our opinion, and to the best of our information and according to the explanations given us, the said Accounts give the information required by the Companies Act 1948, in the manner so required, and give a true and fair view, in the case of the Balance Sheet of the state of the Institute's affairs as at 30 June 1954, and in the case of the Income and Expenditure Account of the excess of Expenditure over Income for the year ended 30 June 1954.

Approved on behalf of the Council: S. F. DOREY, *President*.
J. C. COLQUHOUN, *Honorary Treasurer*.

E. H. JONES, Chairman, Finance and General Purposes Committee.

POPPLETON AND APPELBY,
CHARTERED ACCOUNTANTS, BIRMINGHAM AND LONDON.

THE INSTITUTE OF METALS
INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 30 JUNE 1954

[illegible]

THE INSTITUTE OF METALS
FUND ACCOUNTS FOR THE YEAR ENDED 30 JUNE 1954

ENDOWMENT FUND

1953																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																				
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INDUSTRIAL DONATIONS FUND

	£		£
To Secretarial Expenses and Printing	215	By Balance at 30 June 1953	11,297
" 10-Year Index to <i>Metallurgical Abstracts</i> (Volume 2)	93	Donations (Gross)	9,716
" Special Joint Spring Meeting Expenditure	—	" Interest on Investments	89
" Amount transferred to General Fund, being Excess of Expenditure over Income for the year ended 30 June 1954	5,076		
" Balance at 30 June 1954	15,718		
	<u>£21,102</u>		<u>£25,388</u>
			<u>£21,102</u>

MOND NICKEL FELLOWSHIPS FUND

	£		£
To Grants to Fellows, including Travelling	3,311	By Balance at 30 June 1953	26,527
" Printing, Stationery, Postage, and Publicity	67	Donations Received	7,000
" Bank Charges	3	" Interest on Investments and Bank Interest	559
" Secretarial Expenses	250	" Refund due from Fellow	256
" Balance at 30 June 1954	30,711		
	<u>£31,342</u>		<u>£31,392</u>
			<u>£31,392</u>

CAPPER PASS FUND

	£		£
To Grants	225	By Balance at 30 June 1953	534
" Balance at 30 June 1954	525	Donations Received	200
		" Bank Interest	16
	<u>£750</u>		<u>£750</u>
			<u>£741</u>

W. H. A. ROBERTSON FUND

	£		£
To Expenditure during Year	56	By Donations Received	100
" Balance at 30 June 1954 owing by The Institute of Metals	208	" Balance at 30 June 1953 due by The Institute of Metals	208
	<u>£264</u>		<u>£308</u>
			<u>£308</u>

	1953	£	£		
		<i>GENERAL FUND</i>			
	2,500	£2,500	3% Savings Bonds 1960/70, at cost	.	2,500
	3,000	£3,000	Savings Bonds 1965/75, at cost	.	3,000
	1,010	£1,010	2½% Treasury Stock, 1975 or after, at cost.	.	1,010
	4,734	£4,359	4% Consolidated Stock, at cost	.	4,734
	5,057	£5,000	2½% National War Bonds 1954/56, at cost	.	5,057
	500	£500	2½% Defence Bonds, at cost	.	500
	162	£150	£1 War Savings Certificates (see Note 1)	.	162
	829	£795	6s. 0d. 4% Consolidated Stock (see Note 2)	.	829
17,792					17,792
			<i>Note 1.</i> At cost plus accrued interest to 22.11.50.		
			<i>Note 2.</i> Transferred at Market Value on 22.11.50 from the War-Time Emergency Fund to the General Fund.		
		<i>ENDOWMENT FUND</i>			
	525	£525	2½% Defence Bonds, at cost	.	525
	1,285	£1,285	3% Savings Bonds 1960/70, at cost	.	1,285
	19,482	£17,926	5s. 1d. 4% Consolidated Stock, at cost	.	19,482
21,292					21,292
		<i>INDUSTRIAL DONATIONS FUND</i>			
	950	£950	3% Funding Stock 1966/68, at cost	.	950
	1,000	£1,012	2s. 9d. 4% Funding Stock 1960/90, at cost	.	1,000
	—	£4,956	8s. 10d. 2½% National War Bonds 1954/56, at cost	.	4,984
1,950					6,934
		<i>MOND NICKEL FELLOWSHIPS FUND</i>			
	7,550		Woolwich Equitable Building Society	.	10,550
	1,250		Co-operative Permanent Building Society	.	1,250
	3,500		Halifax Building Society "D" Shares	.	—
	5,000		Abbey National Building Society	.	5,000
17,300					16,800
£58,334					£62,818

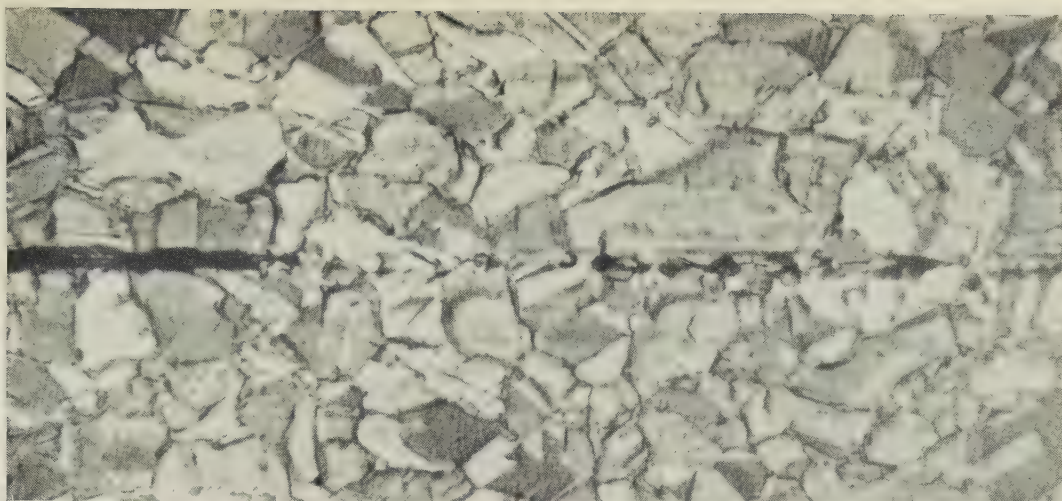


FIG. 2.—Welding of Two Copper Wires While in Close Contact During Annealing. $\times 600$.



FIG. 3.—Dark Stain Produced on Certain Parts of a Reel of Copper Wire During Storage.



FIG. 4.—Fracture of Copper Winding Wire Associated with Deterioration by Gassing Which Occurred in the Hot Bending Operation.



FIG. 5.—Springiness Testing Machine of the Mandrel Type.

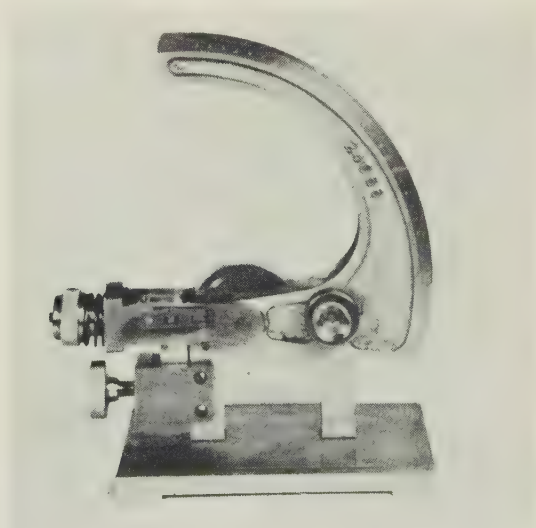
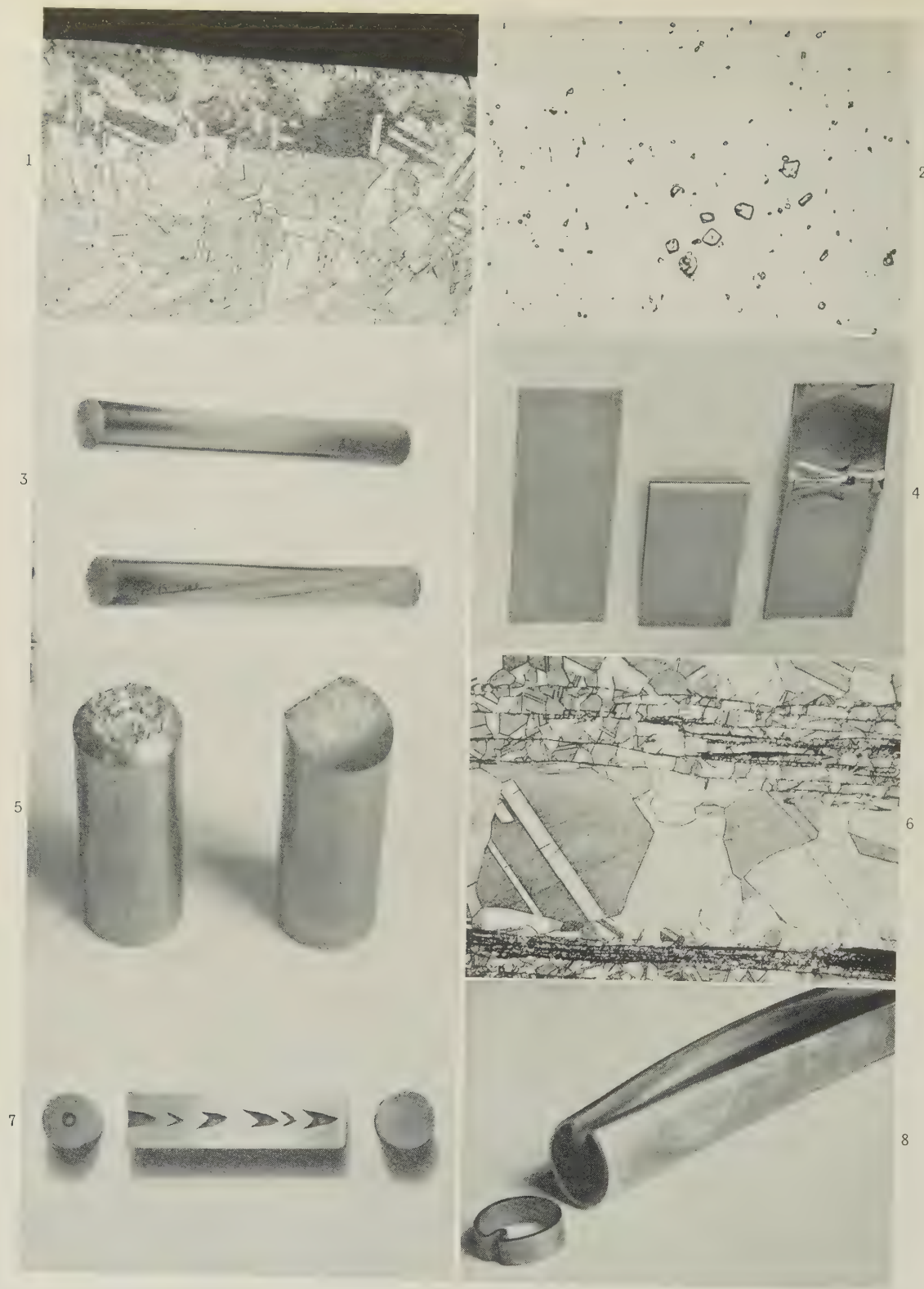


FIG. 6.—Moorhouse Springback Testing Machine, Showing Position at the Completion of Test.



- FIG. 1.—Chromium Copper Rod Showing Oxidized Layer After Heat-Treatment in an Oxidizing Atmosphere. $\times 100$.
 FIG. 2.—Microstructure of Chromium Copper After Solution-Treatment at 1030°C . for 30 Min., Showing Undissolved Coarse Particles of Chromium. $\times 600$.
 FIG. 3.—Rolled and Drawn Phosphor Bronze Rod Subjected to a Twist Test Which Reveals Rolling Defects. $\times 1\frac{1}{2}$ approx.
 FIG. 4.—Phosphor Bronze Strip Before and After Bend Test, Revealing Sub-Surface Blisters. $\times 1$ approx.
 FIG. 5.—Defective Extruded Silicon Brass Rod. (Left) Fracture by nicking and breaking. (Right) Fracture by shearing. $\times 1\frac{1}{2}$ approx.
 FIG. 6.—Longitudinal Section of Rod, as in Fig. 5, Showing Internal Defects. $\times 100$.
 FIG. 7.—Longitudinal Section of Tellurium Copper Rod, Showing Fractured Centre and Two Cross-Sections of the Same Rod. $\times 1$ approx.
 FIG. 8.—Fold in Copper Housing Tube Revealed by Hydraulic Test. $\times 1$ approx.

LIGHT ALLOY DROP-FORGINGS



FIG. 1.—A Partly Made and a Completed Forging with Varying Radii at Base of Ribs.

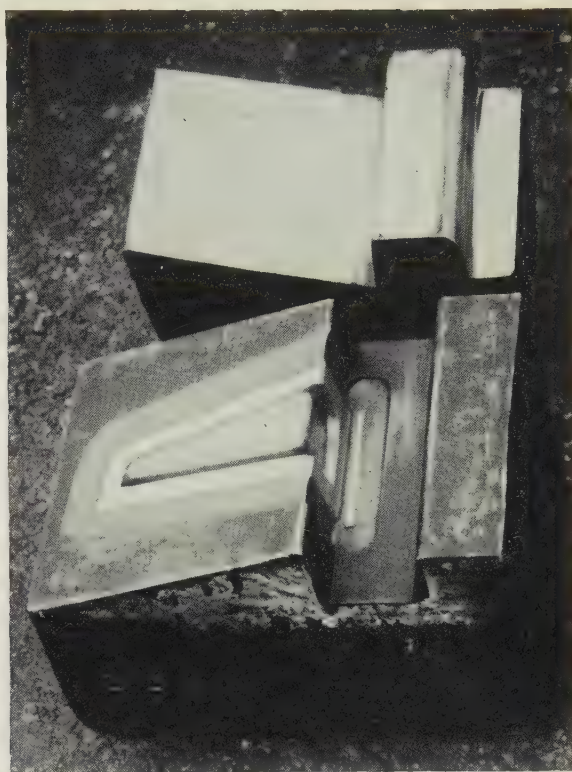


FIG. 4.—Forging Dies with "Stepped" Parting-Line.



FIG. 2.—Flash-Line Cracks Due to Inadequate Radius.



FIG. 3.—Forging Made in Dies Having "Stepped" Parting-Line to Give Continuous Fibre Bent Through an Angle of 112° .

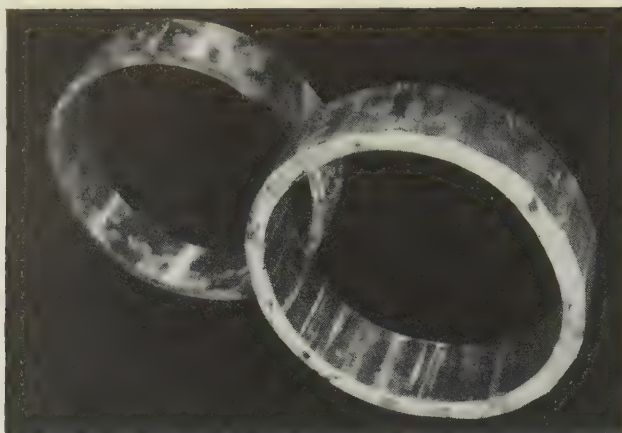
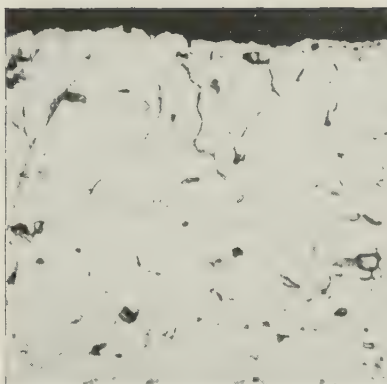
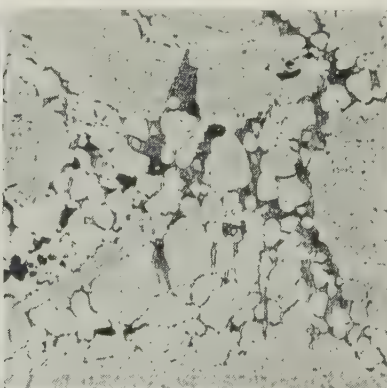


FIG. 5.—Mandrel-Forged Rings in Magnesium Alloy ZW3.

MICROSTRUCTURES OF ALUMINIUM ALLOYS

FIG. 6.—Local Overheating Adjacent to Flash-Line Cracks in L.65 Alloy Forging Made at 480° C. Etched in 0.5% HF. $\times 600$.FIG. 7.—Coarse Intermetallic Compounds in 2-in.-Dia. L.65 Bar Extruded Through Multi-Hole Die. Etched in 0.5% HF. $\times 30$.FIG. 8.—Finer Intermetallic Compounds in 2-in.-Dia. L.65 Bar Extruded Through Single-Hole Die. Etched in 0.5% HF. $\times 30$.FIG. 9.—Part of Fracture in Transverse Tensile Test-Piece from D.T.D.683 Forging. Etched in warm 10% NaOH. $\times 40$.FIG. 10.—Series of Folds Formed in Radius Which Was Too Small. Etched in 0.5% HF. $\times 40$.FIG. 11.—Severe Overheating in D.T.D.364 Extruded Bar. Etched in 0.5% HF. $\times 40$.

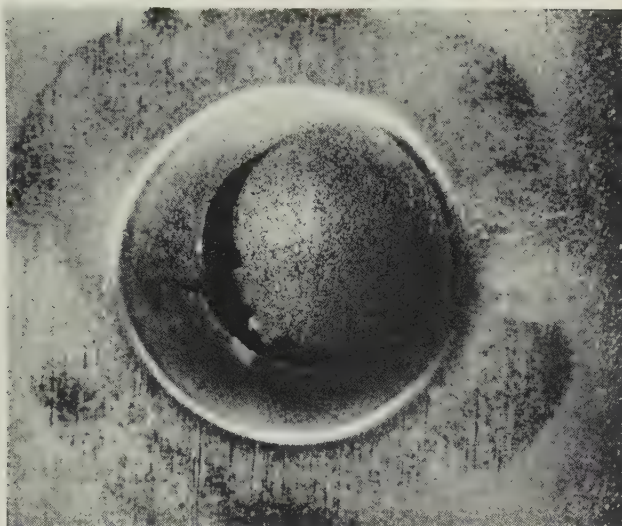


FIG. 1.—Intergranular Pickle Attack in Nickel-Chromium Alloy Sheet (D.T.D.703).

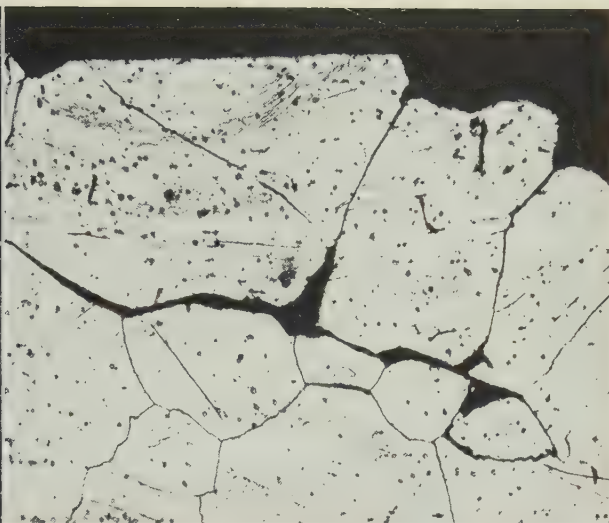


FIG. 2.—Microsection of Material Shown in Fig. 1. $\times 100$.



FIG. 3.—Pitting on End of Nickel-Chromium Alloy Bar (D.T.D.747) after Etching in Boiling Hydrochloric Acid.

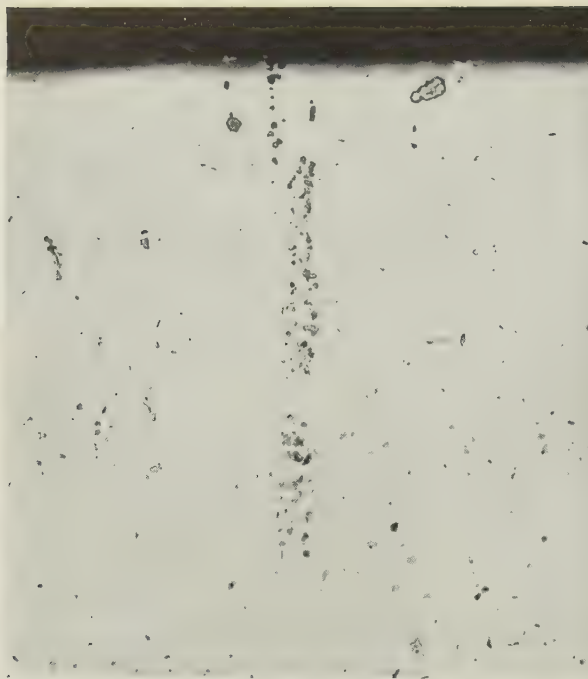


FIG. 4—Section Through Bar Shown in Fig. 3 Before Etching.
× 200.

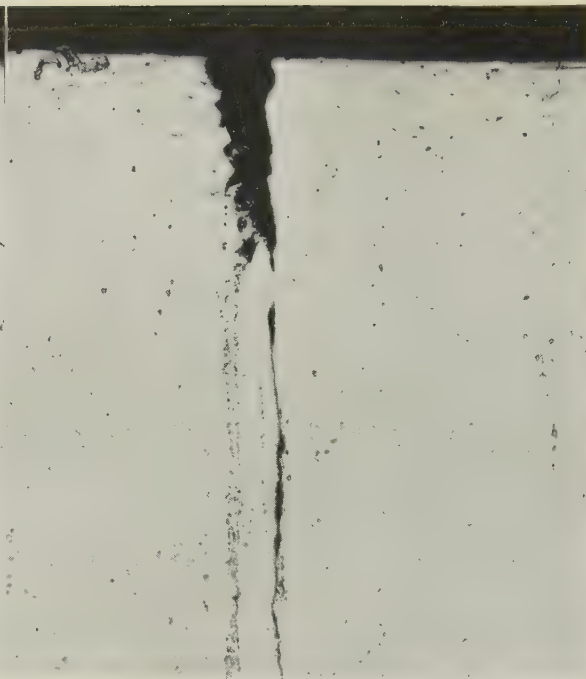


FIG. 5—As Fig. 4, After Etching. × 75.

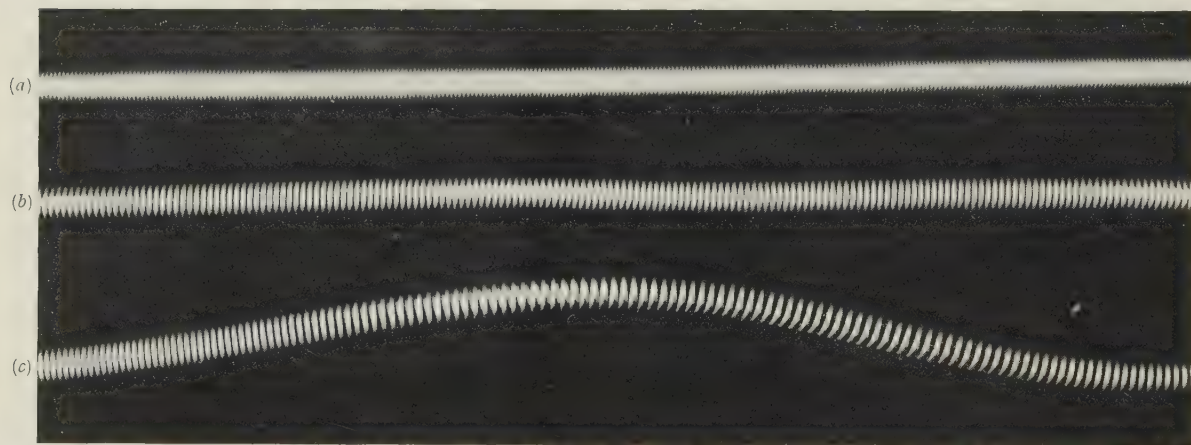


FIG. 6—Spiralling Test for Nickel-Chromium Heating-Element Wires.
(a) Unstretched. (b) Good. (c) Bad.

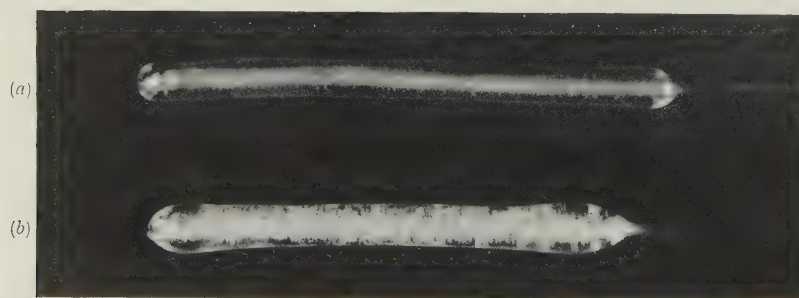


FIG. 7.—Test for Gas-Free Nickel.
(a) Gas-free. (b) Gassy.

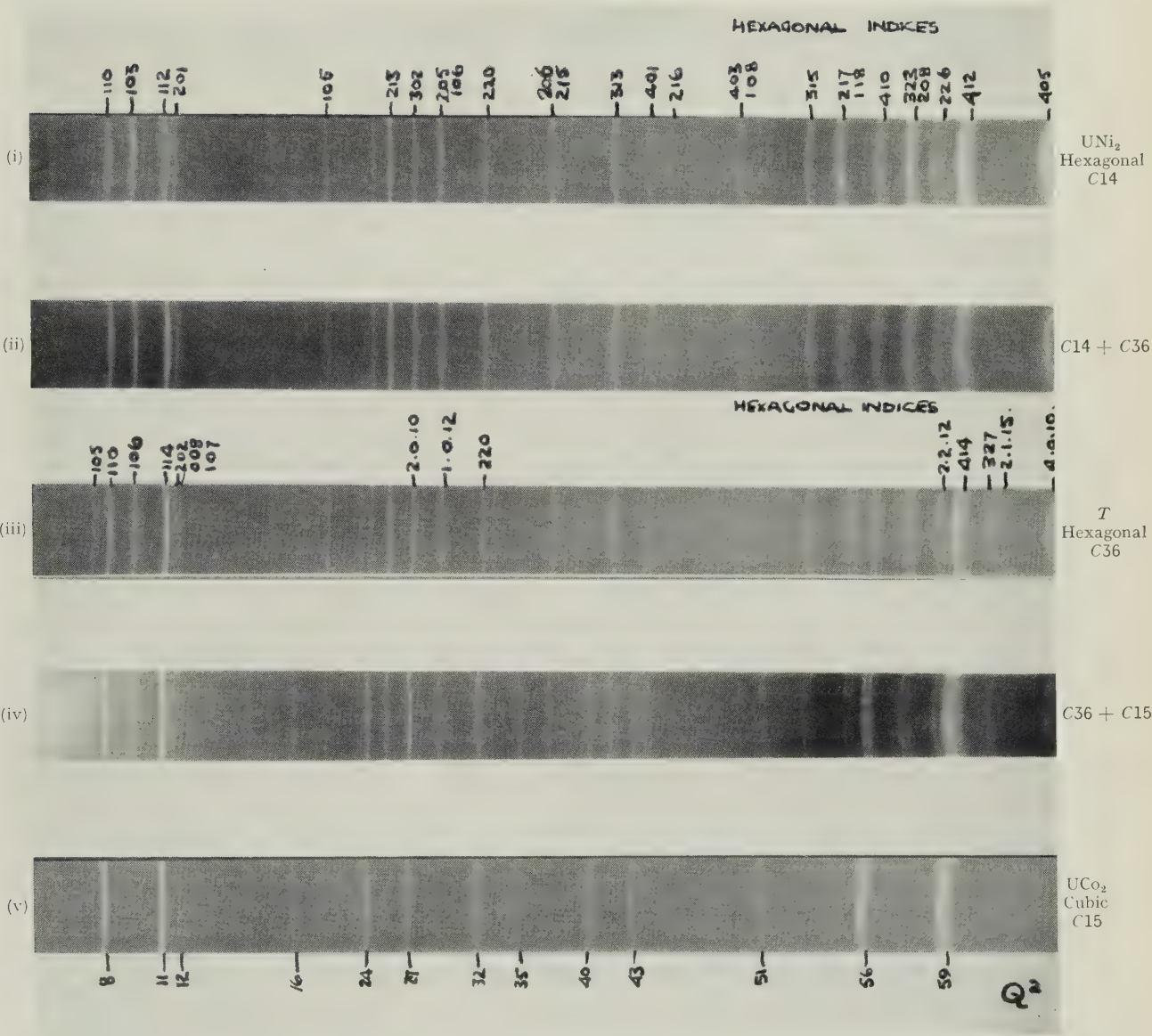


FIG. 2.—Debye-Scherrer Films of Alloys at Compositions Across the Pseudo-Binary System $\text{UNi}_2\text{-UCo}_2$. Photographs taken using $\text{CoK}\alpha$ radiation.

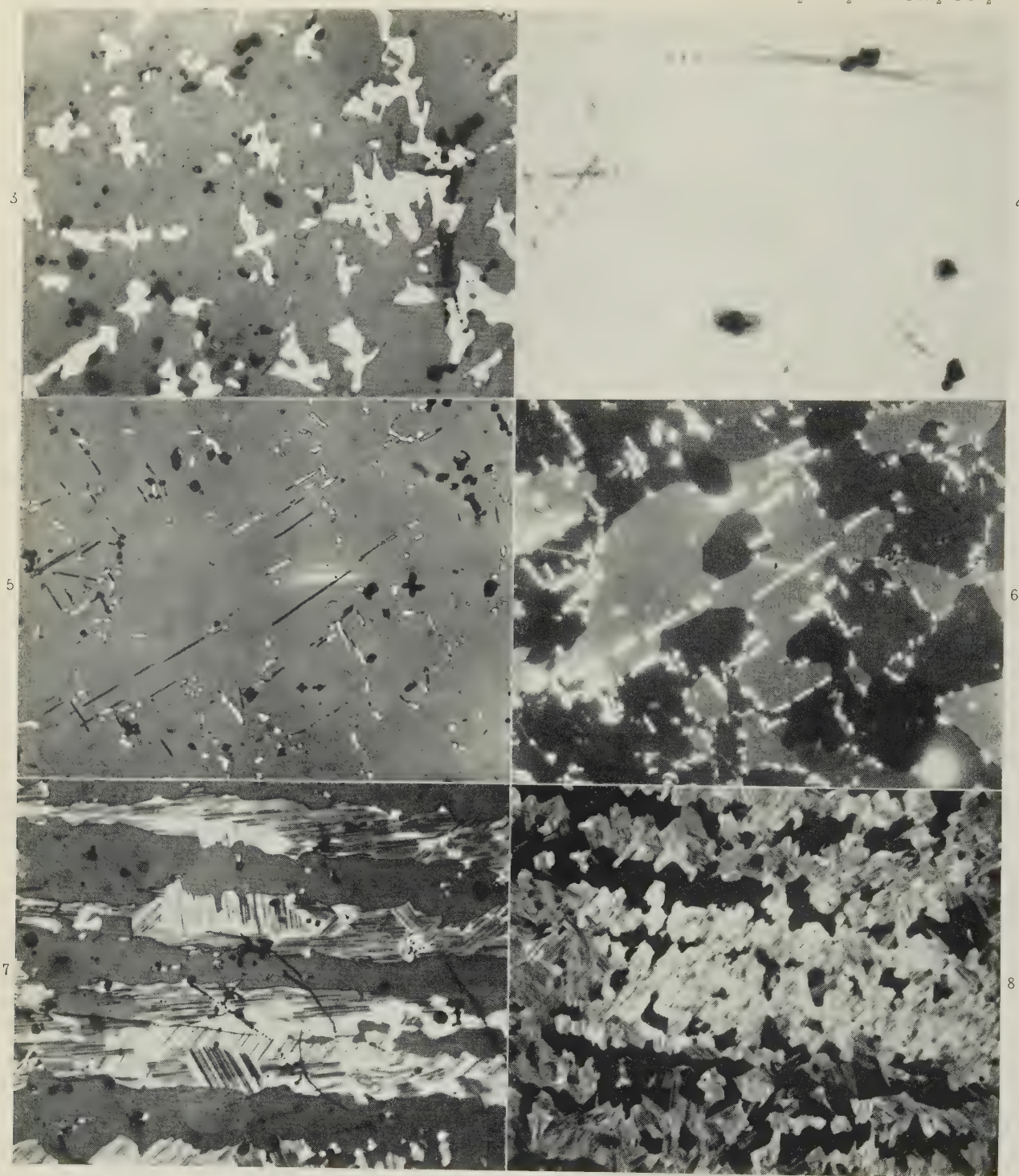
PHOTOMICROGRAPHS ILLUSTRATING LAVES PHASES FOUND IN PSEUDO-BINARY SECTIONS $\text{UNi}_2\text{-UFe}_2$ AND $\text{UNi}_2\text{-UCo}_2$.

FIG. 3.—13.9 At.-% Fe, Quenched from 900° C. UFe_2 white; T_{Fe} half-tone; etched-out oxide, &c., black. $\times 250$.

FIG. 4.—15.3 At.-% Co, Quenched from 700° C. Two phases believed to be oxides or nitrides in T_{Co} . The darker phase occurs in uranium. Unetched. $\times 500$.

FIG. 5.—8.9 At.-% Co, Quenched from 700° C. UNi_2 half-tone; X (U-Ni) white (or dark needles where not resolved); etched-out oxide black. $\times 250$.

FIG. 6.—Same Field as Fig. 5, but with Crossed Polars, Showing Grain Contrast. $\times 250$.

FIG. 7.—10.8 At.-% Fe, Quenched from 700° C. UNi_2 dark; T_{Fe} light, showing precipitation of UNi_2 ; X (U-Ni) small white particles mainly occurring in UNi_2 ; oxide and cracks black. $\times 250$.

FIG. 8.—11 At.-% Fe (Nominal), Quenched from 900° C. UNi_2 dark; T_{Fe} half-tone, showing precipitation of UNi_2 ; etched-out oxide black. $\times 250$.

Etching reagent: oxalic acid in water and glycerol.

MICROSTRUCTURES OF URANIUM-ZIRCONIUM ALLOYS.

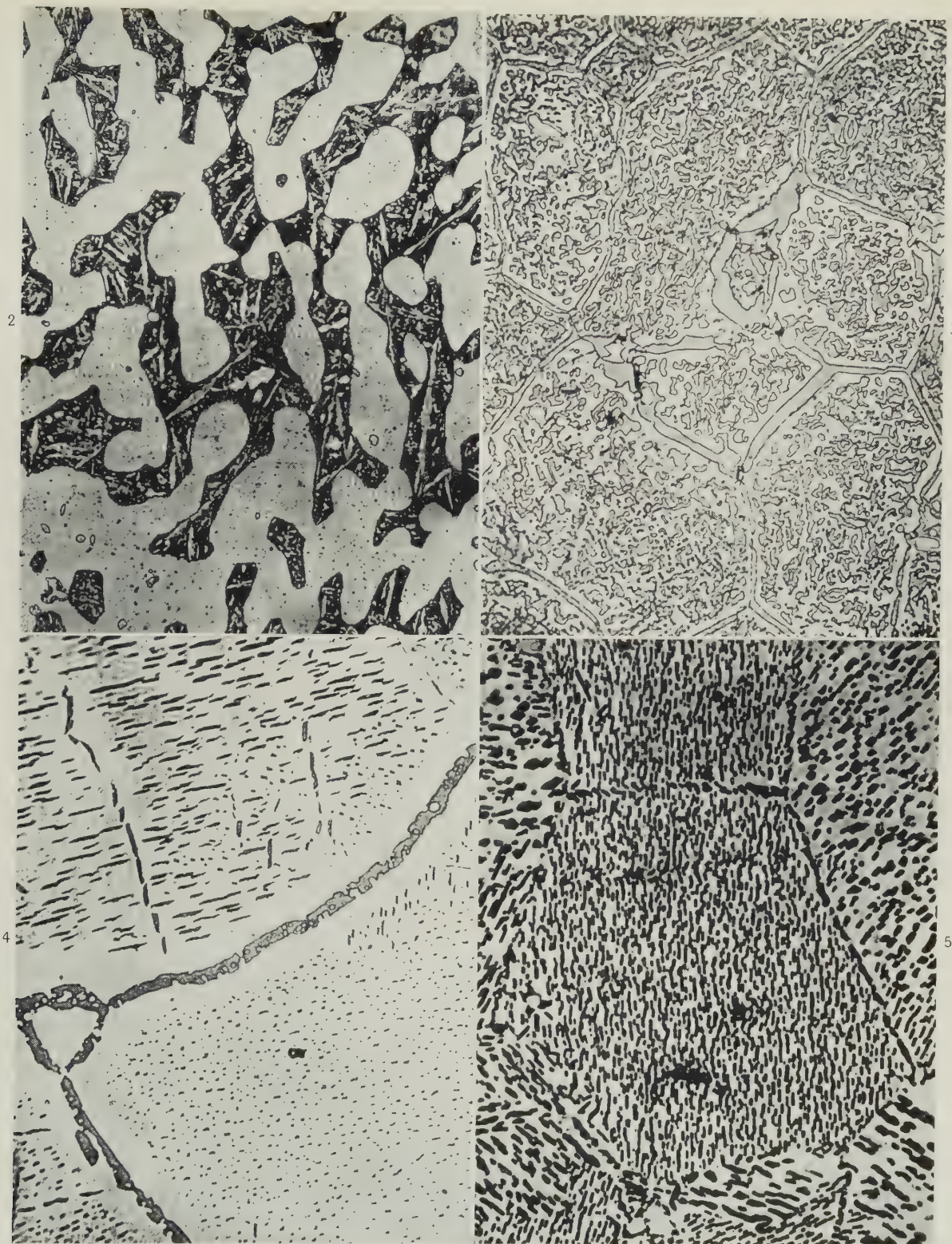


FIG. 2.—4.0 At.-% Zirconium, Water-Quenched from 724° C. $\times 300$.

FIG. 3.—37.2 At.-% Zirconium, Water-Quenched from 712° C. $\times 400$.

FIG. 4.—50.3 At.-% Zirconium, Water-Quenched from 675° C. $\times 600$.

FIG. 5.—50.3 At.-% Zirconium, Water-Quenched from 650° C. $\times 500$.

Figs. 2 etched in 50% nitric acid + 50% acetic acid.

Figs. 3-5 etched in 10% potassium hydroxide + 10% potassium ferrocyanide in water.

STEPS IN CONSTRUCTION OF RAMMED MONOLITHIC REFRACTORY LINING.



FIG. 3.—Showing Asbestos Millboard Facing of the Offtake Bath Centre Wall, Just Installed.

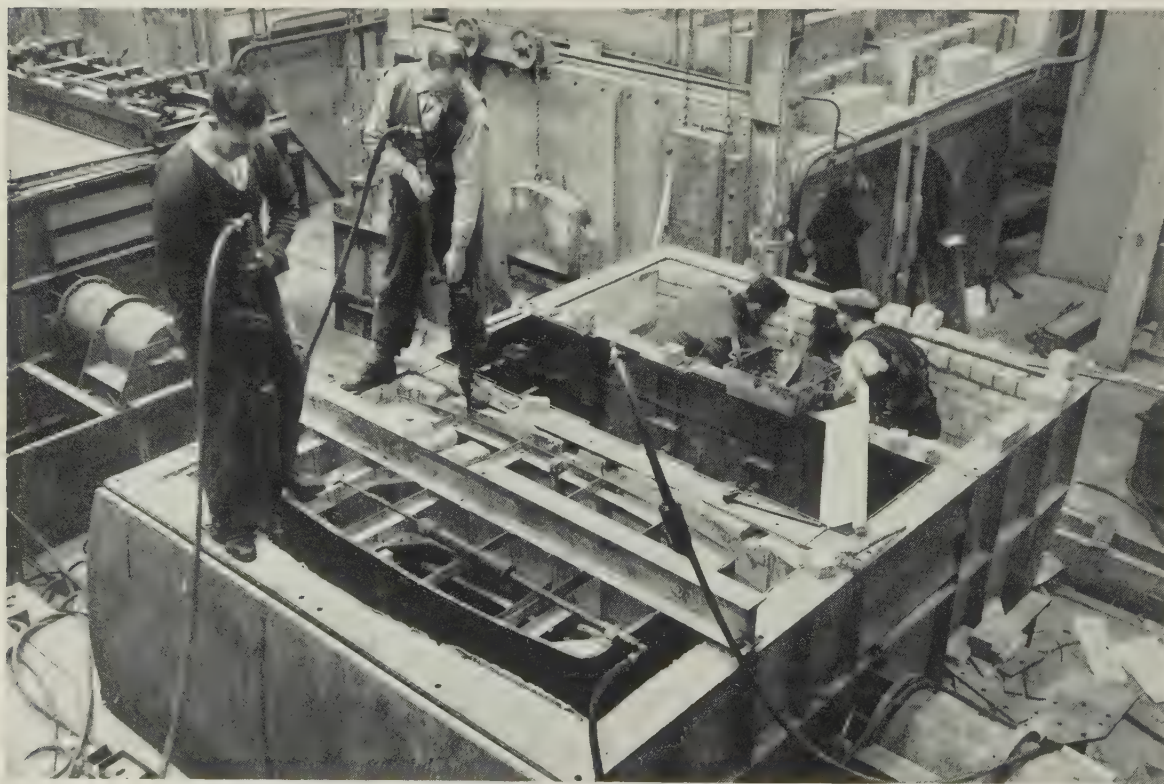


FIG. 4.—Showing Ramming in Progress on the Charging-Bath Walls, and Upper Insulation Brickwork in Offtake Bath Before Facing with Asbestos Millboard.

SEQUENCE OF OPERATIONS IN FORMING RAMMED LINING OF LOW-FREQUENCY INDUCTION FURNACE.

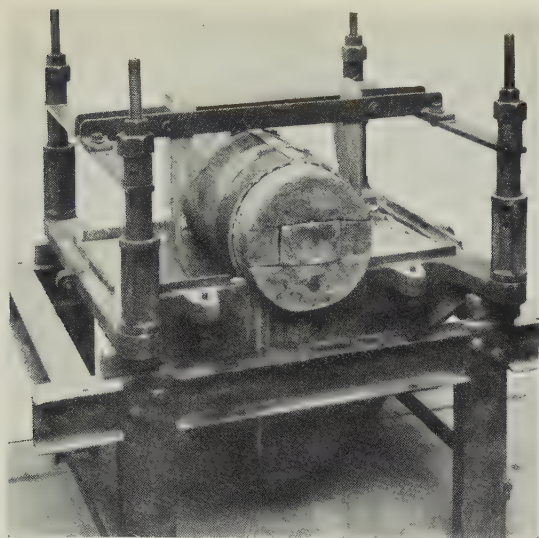


FIG. 4.—Preliminary Alignment of Secondary Channel and Primary Coil Formers.

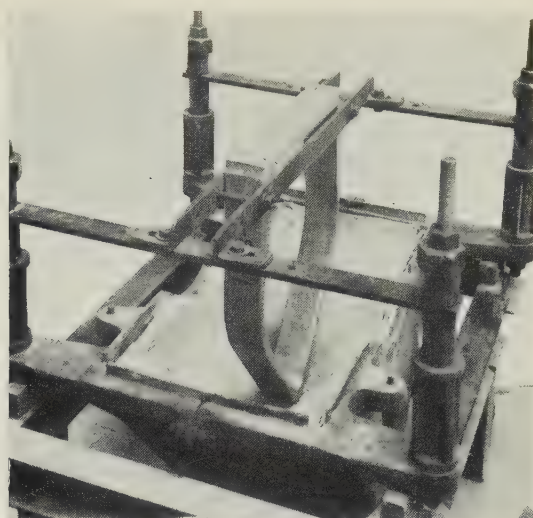


FIG. 5.—Ramming Completed to Apex of Channel Former.

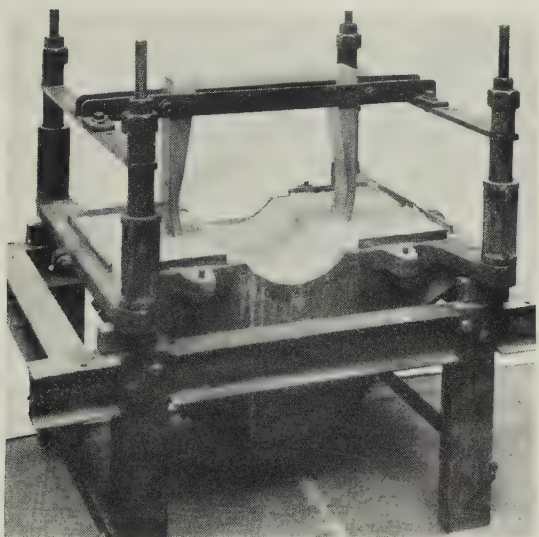


FIG. 6.—Ramming of Lower Part of Furnace Casing Completed and Lining Cut Away to Accommodate Primary Coil Former.

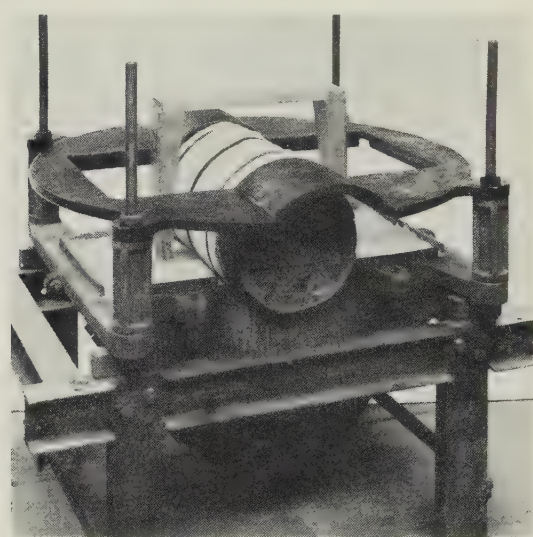


FIG. 7.—Primary Coil Former in Position and Earth Shield Covered with Thin Asbestos Sheet.

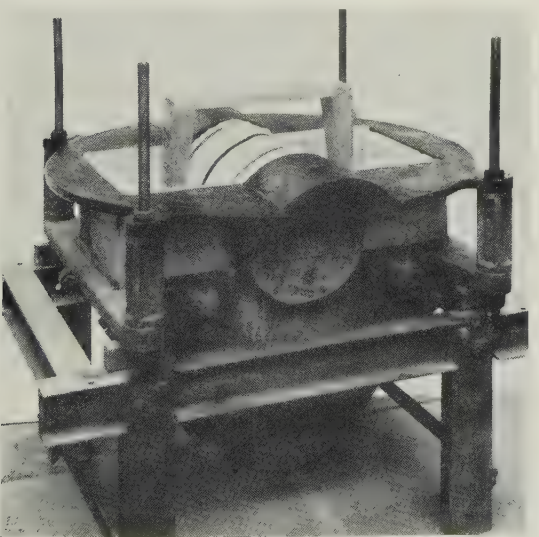


FIG. 8.—View Showing Location of Sindanyo Boards.

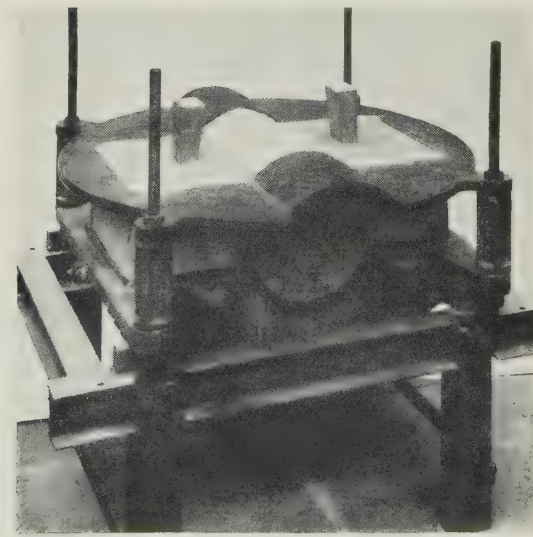


FIG. 9.—Ramming Completed to Furnace-Casing Plate.

SEQUENCE OF OPERATIONS IN FORMING RAMMED LINING OF LOW-FREQUENCY INDUCTION FURNACE.

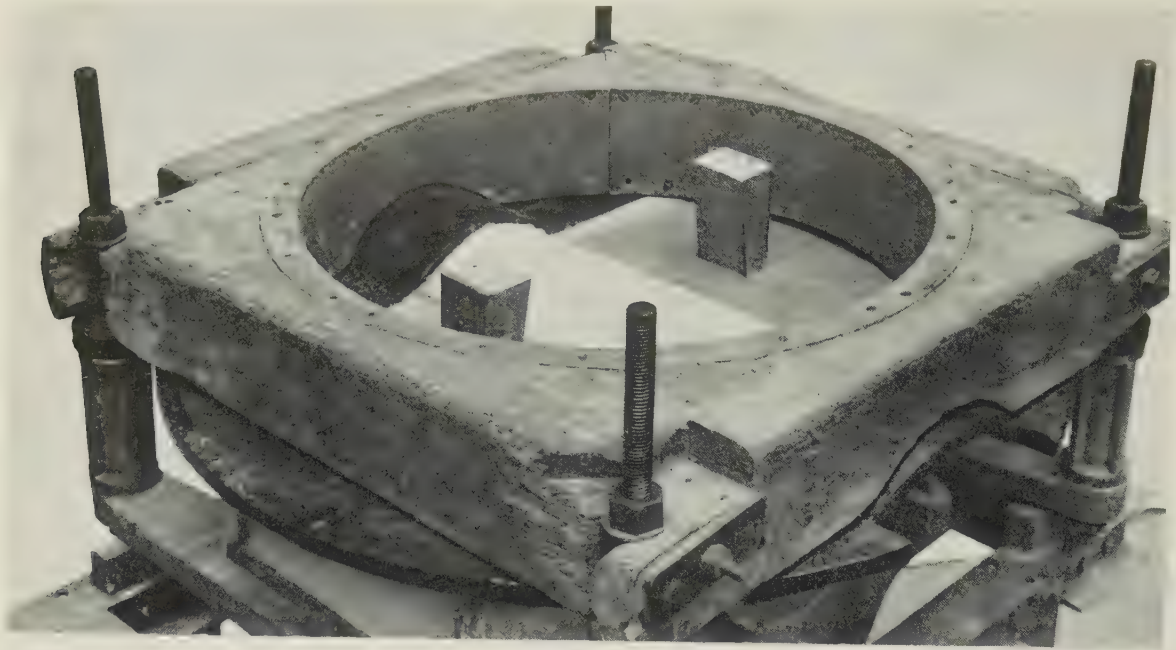


FIG. 10.—Furnace-Hearth Former Placed in Position.

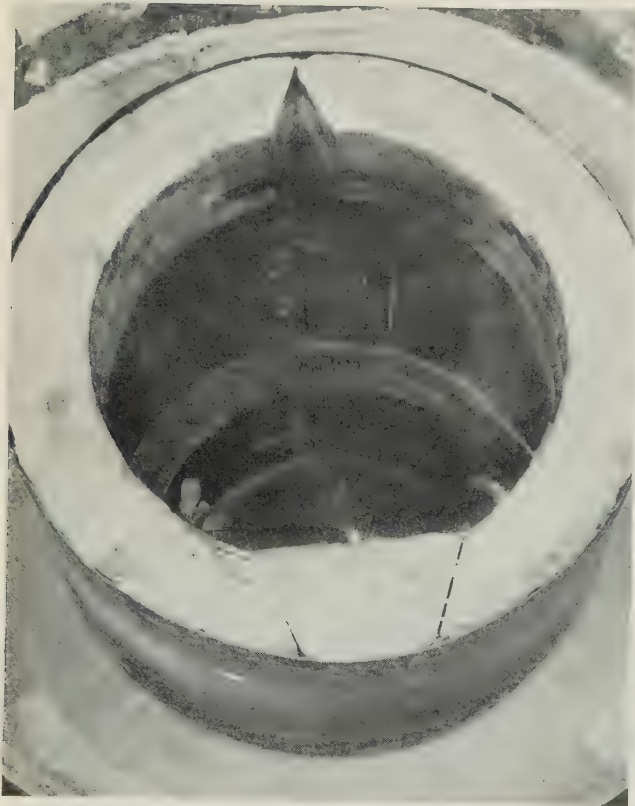


FIG. 11.—Ramming Completed to Level of Furnace Hearth and Body Casing and Wooden Body Former Fixed in Position.

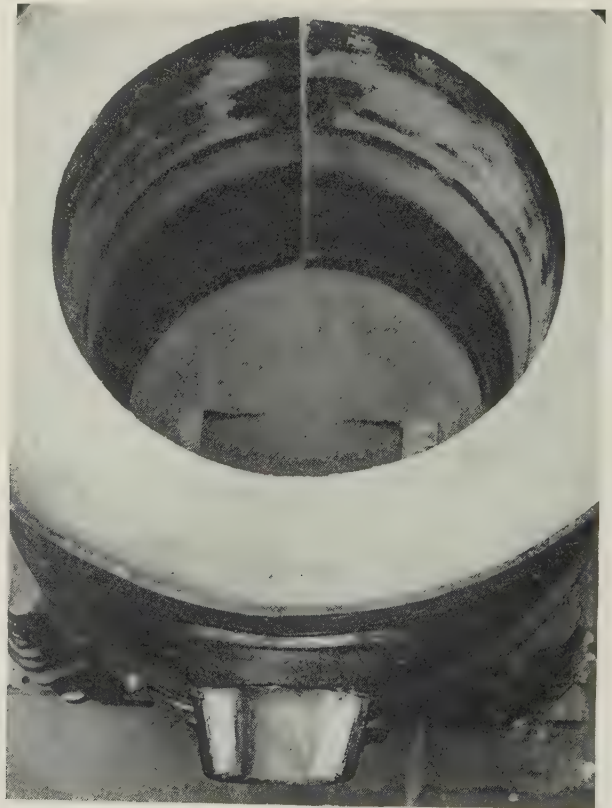


FIG. 12.—Ramming of Furnace Completed and Body Former Removed.

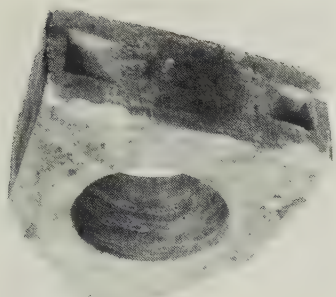


FIG. 13.—Transformer Unit Constructed Separately by Side Ramming.

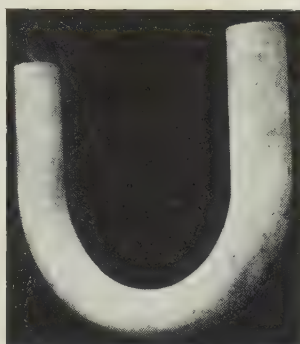


FIG. 14.—U-Shaped Alumina Tube Suitable for Use in Construction of Lining of Low-Frequency Induction Furnace.



FIG. 15.—V-Shaped Silicon Carbide Tube Suitable for Use in Construction of Lining of Low-Frequency Induction Furnace.

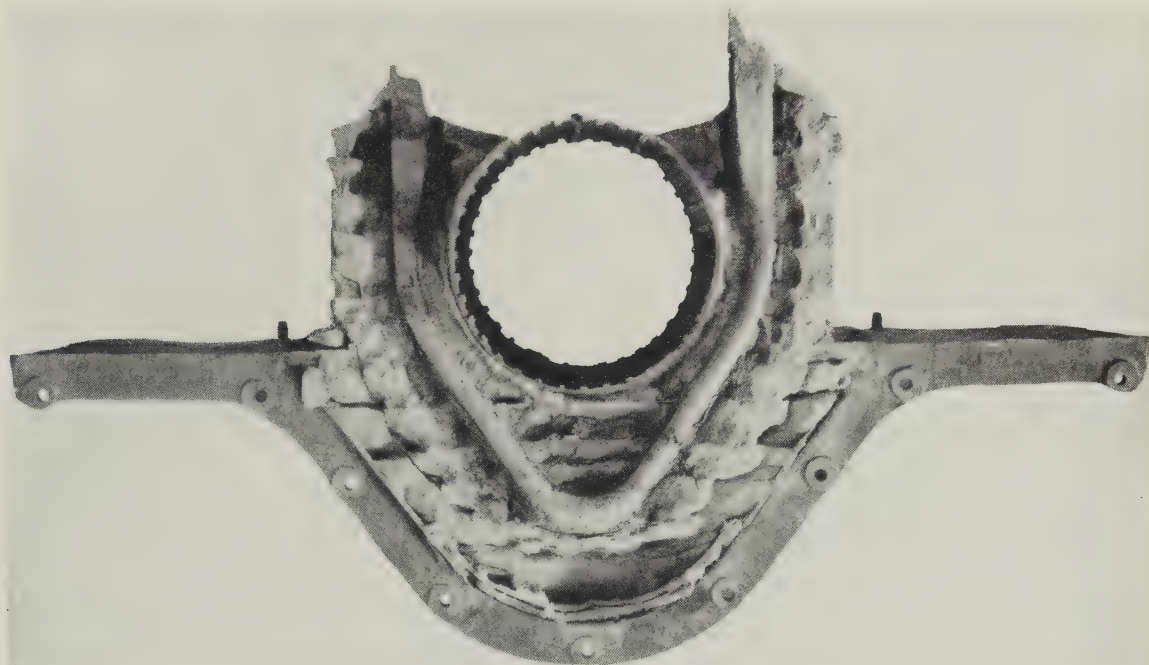


FIG. 16.—Cross-Section through Transformer Unit of Furnace Used for Melting Leaded Brass, Showing Example of Metal Penetration Between Incompletely Bonded Ramming Layers, and a Fracture of the Metal in the Secondary Channel Due to Contraction during Uncontrolled Freezing.



FIG. 17.—Enlarged View of Lining Illustrated in Fig. 16, in the Area of the Apex of the Secondary Channel.

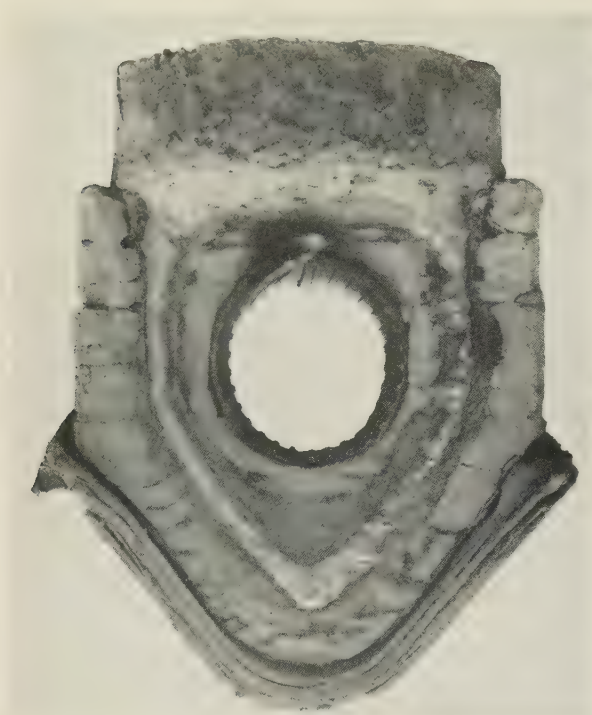


FIG. 18.—Cross-Section through Transformer Unit of Brass Melting Furnace, Illustrating (upper part of photograph) Penetration of Metal through the Hearth of the Furnace to the Earth Shield.

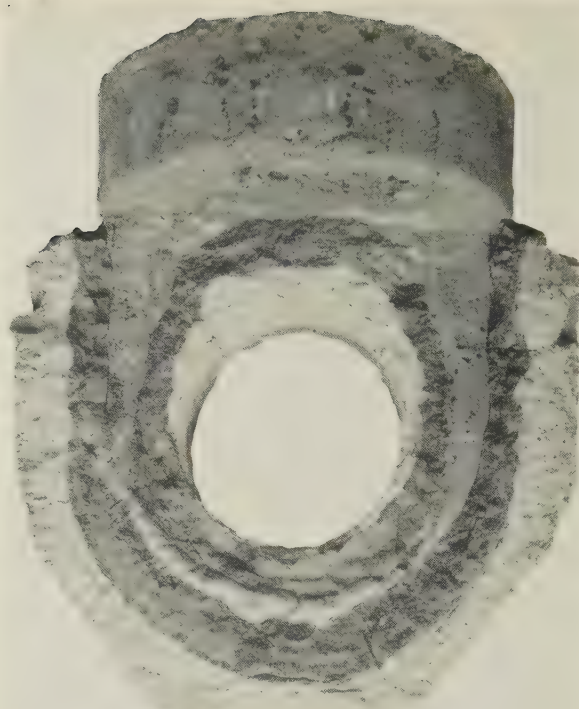


FIG. 20.—Section through Transformer Unit of Furnace Lined with Siliceous Refractory and Used for Melting Phosphorus-Deoxidized Copper, Showing Fracture of the Metal in the Secondary Channel Due to Formation of Local Restriction.

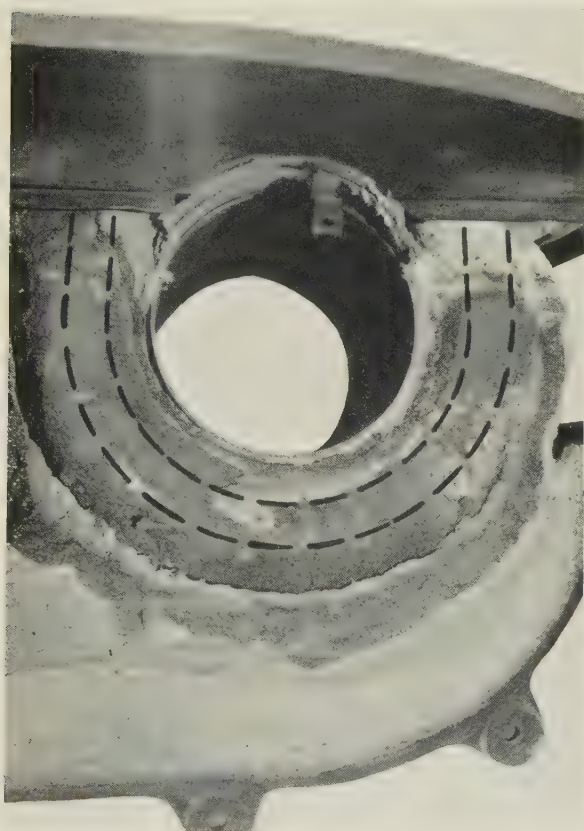


FIG. 19.—Cross-Section through One Transformer Unit of Russ-Type Low-Frequency Induction Furnace Lined with Siliceous Refractory, Showing Gross Channel Enlargement After Melting Approximately 200 Tons of Cupro-Nickel. The outline of the original channel is marked for comparison.



FIG. 21.—Residual Heel of Metal in Lower Part of Furnace and Channel Shown in Fig. 20, after Removal of Refractory.

ATTEMPTS TO IMPROVE ALUMINIUM REDUCTION SINCE HÉROULT AND HALL*

1599

By PROFESSOR DR.-ING., DR.MONT.H.C. A. VON ZEERLEDER,† MEMBER

SYNOPSIS

A survey is given of the various attempts made during the last sixty years to find an improved method of producing aluminium on a commercial scale. It is concluded that none can compete economically with the most modern version of the Hall-Héroult-Bayer process.

I.—INTRODUCTION

THE Centenary of the first production of aluminium on an industrial scale by Sainte-Claire Deville in France affords an appropriate occasion for a review of technical developments in this field.

The concentration of aluminium in the earth's crust, 8.1%, is the highest of all the technically important metals. At 196 cal./g.-atom, its oxidation energy is the third highest after silicon and titanium, thus explaining the difficulty of thermal reduction of aluminium compounds. Last, but not least, aluminium has an electrolytic potential with reference to hydrogen of -1.7 V.; only magnesium has a potential more negative than this, the other metals of technical importance lying more on the positive side. This involves difficulties in its electrolytic reduction.

aluminium chloride vapour into contact with molten potassium, which resulted in a better control of the reaction. This method formed the basis of Sainte-Claire Deville's attempts, which in 1854 culminated in the first industrial process for the production of aluminium. Sodium was substituted for the expensive potassium, and the stable sodium aluminium chloride for the extremely hygroscopic aluminium chloride.

Between 1855 and 1888 there was produced in Sainte-Claire Deville's factories in France, approximately 50 tons of aluminium. Fig. 1 is a sketch of the apparatus used. The price fell from 300 francs (£12) per lb. in 1859 to 66 francs (£2 12s.) in 1888. Some aluminium was produced between 1886 and 1890 at Hemelingen, near Bremen, by reduction of cryolite with magnesium.

II.—HÉROULT-HALL REDUCTION PROCESS

Turning to the electrolytic-reduction method, still in use, the electrolytic preparation of aluminium had been proposed by Bunsen and by Sainte-Claire Deville as early as 1854. The electric dynamo as a cheap source of electric power had, however, not then been invented, and no industrial application of these proposals could therefore be made. Fig. 2 (a)-(d) illustrates the striking similarity between the cell suggested by Sainte-Claire Deville at that time and the one subsequently developed by Héroult. Patents were applied for almost simultaneously by Héroult in France and by Hall in America, in 1886.

The process involves the electrolysis at about 950° C. of a solution of alumina (Al_2O_3) in molten cryolite ($\text{AlF}_3 \cdot 3\text{NaF}$); metallic aluminium is deposited at the cathode, while oxygen forms at the carbon anode and is dispersed in the form of carbon monoxide and dioxide (Fig. 2 (e)). Recourse to electrolysis of a

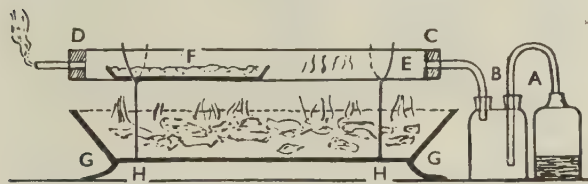


FIG. 1.—Apparatus Devised by Sainte-Claire Deville for the Reduction of Aluminium Chloride, and Used at the Salindres Foundry (1855–88).

KEY.

- A. Hydrogen generator.
- B. Bottle containing calcium chloride, for drying the gas.
- C–D. Bohemian glass tube, containing aluminium chloride at (E) and a tray of sodium at (F).
- G–G'. Chafing dish containing burning charcoal.
- H–H'. Wires supporting the tube.

The first successful attempts to produce aluminium were made by Oersted. In 1825 he obtained metallic flakes of aluminium by the chemical reduction of aluminium chloride with potassium amalgam. Wöhler improved on this procedure, in 1827, by bringing

* Delivered at the Annual Autumn Meeting, Zürich, 9 September 1954.

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molten electrolyte proved necessary because aluminium deposited from an aqueous solution reacts as quickly as it is formed with water to give aluminium hydroxide, with evolution of hydrogen. No ceramic material can resist cryolite at 950°C ., and the walls of the cell must therefore be lined with carbon.

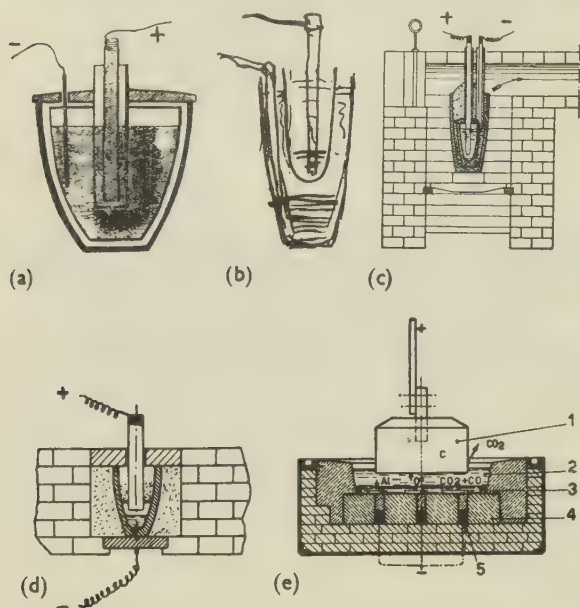


FIG. 2.—Electrolytic Cells for the Production of Aluminium.

- (a) Sainte-Claire Deville's apparatus, 1854.
 (b) Sketch from one of Héroult's notebooks, 1883.
 (c) Sketch from Héroult's first patent, 1886.
 (d) Sketch from his additional patent, 1887.
 (e) Sketch illustrating the chemical reactions in a modern electrolytic cell.

KEY.

1. Carbon anode.
2. Cryolite electrolyte.
3. Molten aluminium as cathode.
4. Precalcined alumina block for bottom lining.
5. Steel bars for electrical connection.

Cryolite and carbon of the necessary purity for the electrodes can be prepared quite easily, but the preparation of pure alumina presents a difficult problem.

III.—PREPARATION OF RAW MATERIALS

1. BAYER PROCESS

The mineral richest in aluminium is bauxite, which ordinarily contains 55–65% Al_2O_3 , 20–25% Fe_2O_3 , and 1–4% SiO_2 (see Table I). The cheapest process of preparing alumina, invented in 1892 by an Austrian, Bayer, and used almost exclusively today, is based on the fact that alumina is readily dissolved by caustic soda of 45° Bé. at 165°C . under a pressure of 6 atm. Insoluble impurities, such as iron, silicon, and titanium, can be separated by filtration leaving the sodium aluminate solution. This filtrate is diluted with water to four times its volume, and precipitation of aluminium hydroxide is initiated by addition of some aluminium hydroxide from an earlier batch. Fig. 3

(a) and (b) illustrates the various stages of the alumina process. The precipitated aluminium hydroxide is separated by decantation and filtration, the filtrate

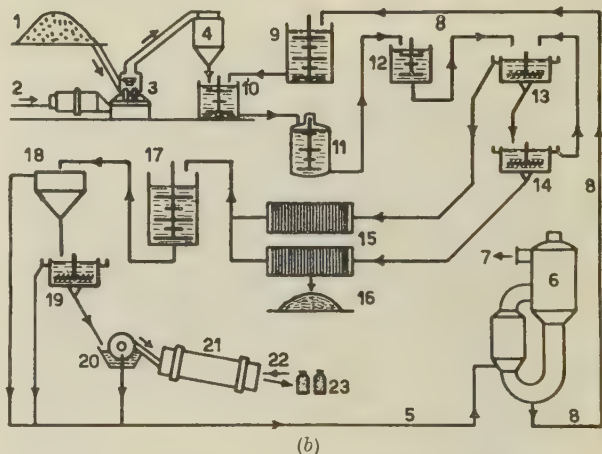
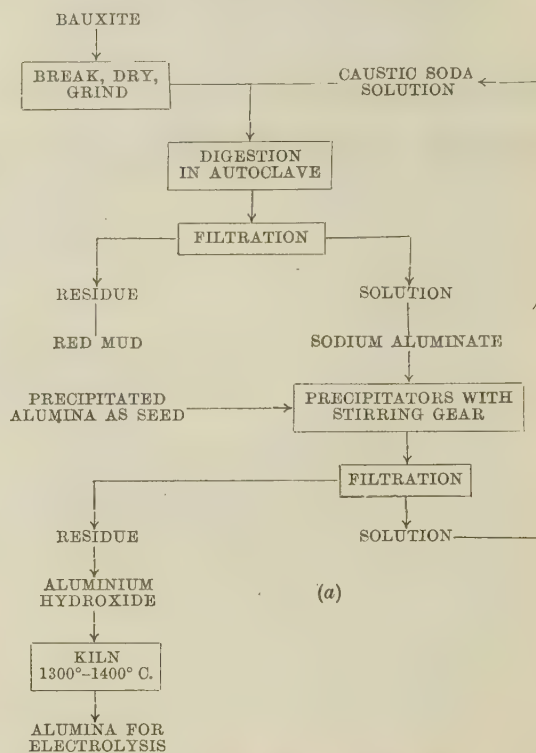


Fig. 3 (a) and (b).—Sequence of Operations in the Bayer Process for the Production of Alumina.

KEY.

1. Bauxite.
2. Gas heating at 350°C .
3. Mill.
4. Autoclave.
5. Dilute caustic soda solution.
6. Evaporator.
7. Vapour.
8. Concentrated caustic soda solution.
9. Container for concentrated caustic soda solution.
10. Mixer.
11. Autoclave.
12. Dilution vessel.
13. First Dorr concentrator.
14. Second Dorr concentrator.
15. Filter.
16. Red mud.
17. Decomposer.
18. Precipitator.
19. Dorr concentrator.
20. Rotary-drum filter.
21. Rotary tube furnace.
22. Heavy oil.
23. Alumina.

being concentrated by evaporation and recycled. The aluminium hydroxide is dehydrated by calcination at 1400°C ., the product being aluminium oxide in its

α modification (Al_2O_3): It is essential that the silica content of the bauxite should be as low as possible, as it reacts with the caustic soda, forming sodium aluminium silicate, which involves loss of both soda and alumina.

Bauxites suitable for the Bayer process are not very plentiful. It is therefore worth while exploring the possibility of using other commoner aluminium-bearing ores, such as clay, kaolin, &c. There are various ways in which this may be achieved: a method might be developed using a different source of alumina or a different electrolyte, or the electrolytic-reduction method might be replaced by one employing a thermal process followed by refining.

2. UTILIZATION OF OTHER SOURCES

(a) Wet Methods

As already stated, bauxite is the ore which is by far the richest in alumina; the comparative figures for kaolin and clay are given in Table I. The use of a

TABLE I.—Composition of Bauxite, Kaolin, and Clay and Consumption in Production of Alumina.

	Bauxite	Kaolin	Clay
SiO_2 , %	1-4	45-65	50-65
Fe_2O_3 , %	20-25	0.8-1.5	1-6
Al_2O_3 , %	55-65	25-38	25-35
Percentage of Al_2O_3 extracted	50	25	22
Amount (kg.) required to produce 1 kg. Al_2O_3	2	4	4.5

poorer ore naturally means that more of it must be treated, in itself a technical and economic disadvantage. The first process tested on a large scale for the production of alumina from other sources was one devised by Serpek (1908). Silica-rich bauxites and other ores, with additions of carbon and nitrogen, were treated in an arc furnace and aluminium nitride was produced. This was decomposed with water to give aluminium hydroxide and ammonia. Although in experiments on a laboratory scale the formation of aluminium nitride proceeded with an acceptably high output, large-scale experiments proved completely unsatisfactory. The rate of cooling of the aluminium nitride was too slow, the nitride decomposing before it had reached a stable temperature level. Output was exceedingly poor and the experiment had to be abandoned.

Other methods which have been attempted include that of Berger and Kuhn, who treated with chlorine gas at $400^\circ\text{--}500^\circ\text{C.}$ a mixture of porcelain clay with three times its weight of pyrites. Aluminium chloride was formed, which could be hydrolysed to give alumina or itself electrolysed.

Svendson treated clay with a solution of ammonium fluoride at 36°C. , a double fluoride of silicon and ammonia being formed. The solution was evaporated, heated to 400°C. and treated with ammonium chloride.

This resulted in the formation of aluminium chloride and fluoride, silica gel being obtained as a by-product. This process might prove economical if a market could be found for the large tonnages of silica gel—three times the weight of the alumina—produced.

Baron Blanc developed a process for the utilization of the large Italian deposits of leucite by treating this ore with hydrochloric acid. It was possible to separate the potassium and aluminium chloride thus obtained by fractional crystallization, the end products being alumina and potassium salts.

The Halvorsen process, an improvement on the Goldschmidt process mentioned below, was intended to make use of labradorite, which is plentiful in Norway. It consisted of a treatment with nitric acid,

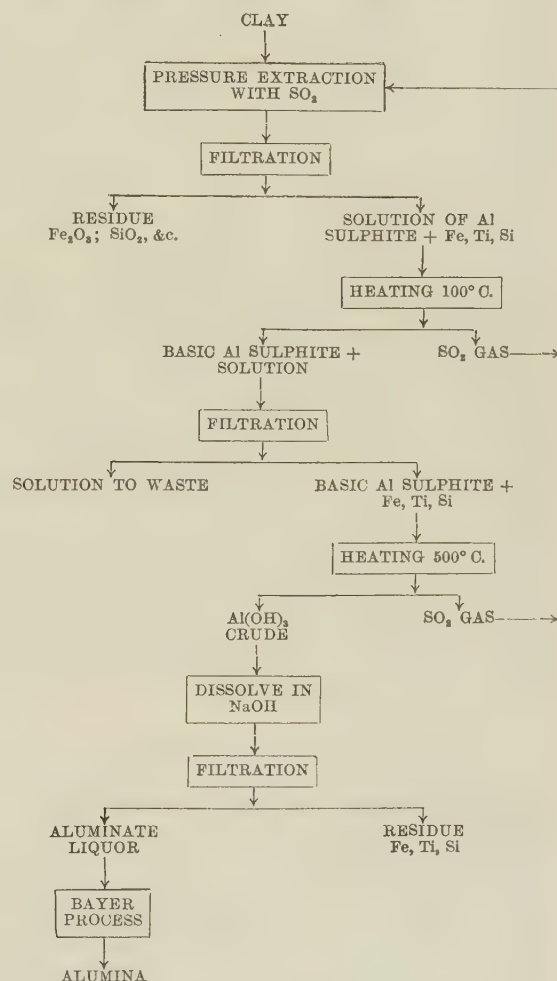


FIG. 4.—Flow Sheet of the S.T. Process for the Electrolytic Preparation of Alumina.

The Buchner method and several others developed by Griesheim-Elektron and I.G. Farbenindustrie were all based on acid treatment of aluminous materials.

The production of pure alumina by means of the S.T. process is illustrated in Fig. 4. By this method, developed in Germany by T. Goldschmidt of Essen and the Vereinigte Aluminiumwerke, clay was calcined

and treated under pressure with an aqueous solution of sulphurous acid. Two of its advantages were the cheapness of sulphurous acid and the fact that apparatus similar to that for the Bayer process could be used. However, up to the present date this process has not yielded alumina of an acceptable purity, making a further Bayer purification treatment essential. Its development, however, represents important progress in so far as it makes possible the use on a large scale of the abundant supplies of clay. This adds to its value in the case of countries poor in bauxite, and in the eventuality of bauxite deposits becoming exhausted in the future.

The Kalunite process employs alunite, a basic potassium aluminium sulphate containing between 15 and 35% of Al_2O_3 . The alunite is calcined and then leached with $\text{H}_2\text{SO}_4 + \text{K}_2\text{SO}_4$. Alum forms and can be isolated by crystallization, transformed to insoluble basic alum, and its SO_3 removed by roasting in an autoclave. The SO_3 is recycled, the K_2SO_4 leached, and the residue, consisting of Al_2O_3 , is filtered off and dried. The first application of this process on an industrial scale has been limited to a capacity of 50 tons of Al_2O_3 /day. Its large-scale use turns on the question of production costs.

In 1943 the U.S. National Bureau of Standards initiated a new process for the production of alumina from clay and kaolinite, which involved the following operations. The raw material was roasted at 700°C . and then treated with 20% hydrogen chloride. At this stage, in addition to the iron and alkali, most of the alumina was in solution. $\text{AlCl}_3 + 6\text{H}_2\text{O}$ was precipitated by evaporation and saturation with hydrogen chloride, then filtered off and washed with hydrochloric acid, which could be subsequently recycled. The alumina obtained was 99.8% pure, with about 0.04% iron oxide and 0.06% silica. As in the case of other alternative methods, alumina prepared by this means cost about twice as much as that prepared by the Bayer technique. It did not therefore prove to be an economic proposition.

(b) Electrothermal Methods

In addition to the above wet processes, considerable importance also attaches to the electrothermal preparation of alumina.

This was first developed by Hall, the American inventor of the electrolytic-reduction method for producing aluminium. He treated bauxite with carbon in an arc furnace, so that electropositive impurities, such as iron, silicon, and titanium, were separated in metallic form. A very hard alumina slag was formed which had to be milled or atomized to make it soluble in molten cryolite and ready for the electrolytic process.

Between 1930 and 1940 an improved modification of this process, suggested by Frary, was in commercial use in Canada. It has, however, since been abandoned, an indication that it could not compete with the Bayer process.

A 15,000-kW. arc furnace with 900-mm. Söderberg

electrodes was developed in Norway for the treatment of bauxite, the energy consumption being 4000–5000 kWh./ton of corundum. Sale to the steel industry of the ferrosilicon produced as a by-product, however, can reduce this to an effective consumption of 3000–4300 kWh./ton. A serious difficulty is presented by the very high melting point of corundum. In 1921 Haglund discovered that its melting point could be lowered from 2050° to 1100°C . by adding 20% aluminium sulphide. His cycle of operations is illustrated in Fig. 5. Bauxite is melted together with

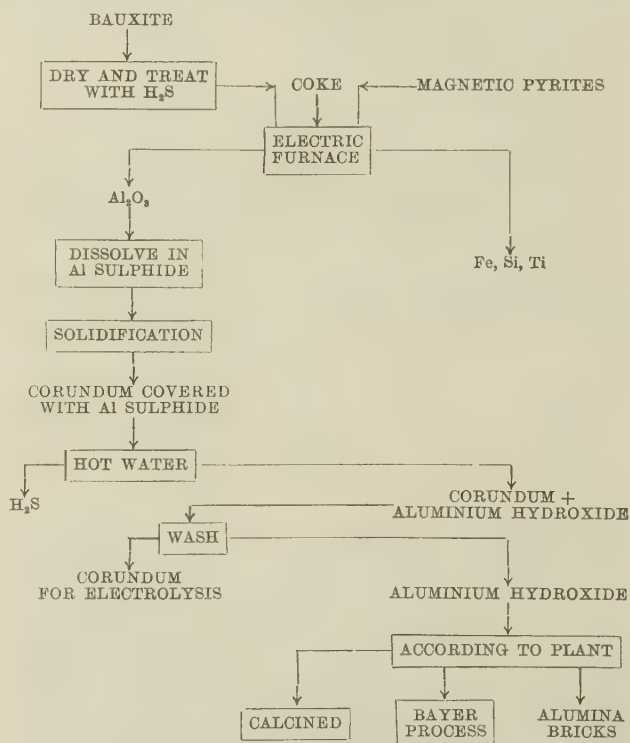


FIG. 5.—Flow Sheet of the Haglund Process for the Electro-thermal Preparation of Alumina.

pyrites and the product leached with water. Hydrogen sulphide is formed which can be recycled. The residue consists of tiny crystals of alumina. As in other cases, however, the alumina made by this process is not of an acceptable purity.

The Haglund process was employed for several years at the Porto Marghera factory of the Montecatini company, near Venice. A serious difficulty encountered was in the control of the titanium content, and leaching with sulphuric acid proved necessary. It was, however, impossible to dispose of the iron produced as a by-product, owing to its high sulphur content, and the project has been abandoned.

The only thermal process which has so far assumed any technical importance is the Pedersen method, used at a plant at Høyanger in Norway. Its successive steps are illustrated in Fig. 6. A mixture of iron ore, coke, lime, and bauxite is melted in an electric furnace. The resulting calcium aluminate slag con-

tains 30–50% Al_2O_3 and 5–10% SiO_2 , with iron of high quality as a by-product.

Because of its high silicon content, this alumina cannot be subjected to the Bayer process, but must be treated with sodium carbonate, leading to the formation of insoluble calcium carbonate and sodium

experience has shown that the preparation of aluminium sulphide of the required purity is not an economical proposition. A further very serious difficulty is presented by the sulphur vapours, which preclude the use of an open cell; gas-tight cells involve considerable inconvenience and expense.

Another possibility is offered by a combination of an electrothermal reduction and an electrolytic-refining process. The first suggestion on these lines was made by Le Chatelier, who worked with Sainte-Claire Deville. He proposed the use of sodium aluminium chloride, with or without the addition of cryolite, as a solvent. With such an electrolyte, electrolysis proceeds at a temperature below the melting point of aluminium, which means that solid cathodes and anodes can be used, as in the refining of copper. A practical attempt to put this project into effect was undertaken by the Société Anonyme pour l'Industrie de l'Aluminium in 1926. The electrolyte used was composed of 70–75% aluminium chloride, 10–12% potassium chloride, and 15–18% sodium chloride, and had a melting point of about 100° C. The electrolysis was conducted at 170–180° C., with an initial current density of 1.5 amp./dm.². With subsequent attack of the anode, the c.d. dropped to 0.5 amp./dm.², while the voltage increased from 0.15 to 0.4 V. (In the alumina/cryolite process, a considerably higher voltage of 4.5 V. and a correspondingly higher energy consumption is involved.) A silico-aluminium anode was used, prepared by thermal reduction, containing 60–70% aluminium and with the lowest possible iron content. With the c.d. and voltage mentioned above even the FeAl_3 was decomposed and the corresponding amount of aluminium recovered. A serious disadvantage of this process is the formation of excrescences on the cathode deposit. This could be overcome only by the addition of about 0.1% lead, which was later removed by vacuum distillation of the molten cathode metal. The aluminium produced was 99.9% pure. In spite of being technically feasible, this process also was discontinued for economic reasons.

Chloride electrolysis has recently been studied again by Professor Grothe and tried out, working with a 1000-amp. cell, in a pilot plant of the Société Anonyme pour l'Industrie de l'Aluminium at Neuhausen, in collaboration with the Vereinigte Aluminiumwerke. Bauxite is treated with chlorine, whereupon iron separates as iron, titanium, and silicon chlorides. The bauxite, now almost iron-free, is then transformed into aluminium chloride. A melt consisting of the aluminium chloride, with 12% MgCl_2 , 35% KCl , and 8% LiCl , is electrolysed at 700° C. making use of the multiple procedure. Molten aluminium is deposited at the bottom of the cell and periodically removed. The chlorine evolved at the anode can be recycled to transform the bauxite to aluminium chloride.

On financial grounds this process, also, is unable to compete with the normal alumina/cryolite electrolysis, as the cost of the aluminium chloride compares very unfavourably with that of alumina.

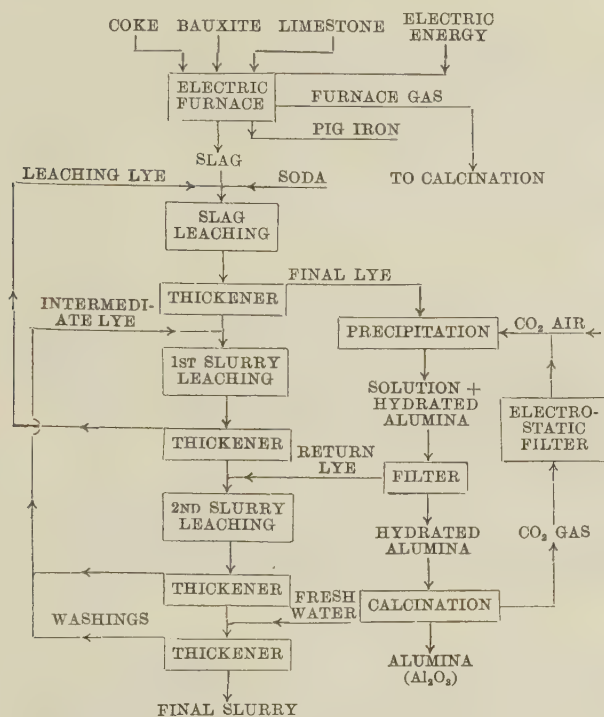


FIG. 6.—Flow Sheet of the Pedersen Process for the Electrothermal Preparation of Alumina.

aluminate. The best results have been achieved with a 3–8% sodium carbonate solution, containing 0.3–0.8% caustic soda. Alumina is precipitated with carbon dioxide, and sodium carbonate is left in solution. None of these methods, however, can compete with the Bayer process.

IV.—ALTERNATIVE ELECTROLYTIC PROCESSES

It has frequently been proposed since 1890 that aluminium sulphide instead of alumina should be electrolysed. Several advantages would accrue if this were done: (1) The consumption of the anode connected with the depolarization of oxygen would be eliminated. (2) The solubility of the sulphide in the electrolyte would be much higher than the solubility of alumina, which is limited to 10% under practical conditions. (3) Electrolysis could be conducted at 850° C., i.e. 100° C. lower than with alumina. (4) Either cryolite or alkali chlorides could be used as the solvent in the electrolyte, thereby making possible the substitution of fire-bricks for carbon in the cell walls. A re-investigation of this process has recently been undertaken by Röntgen and Borchers. My own

V.—ATTEMPTS TO REFINE IMPURE ALUMINIUM

In 1901 Hoopes, an assistant to Hall, undertook experiments with the object of refining impure aluminium, prepared by thermal reduction, in a

process was further improved by Frary and Edwards (Fig. 7 (c)). The anode metal, increased in density by the addition of heavy metals, forms the lowest layer at the bottom of the cell. The electrolyte, which forms the middle layer, consists of cryolite with an addition of barium fluoride to raise its density. The

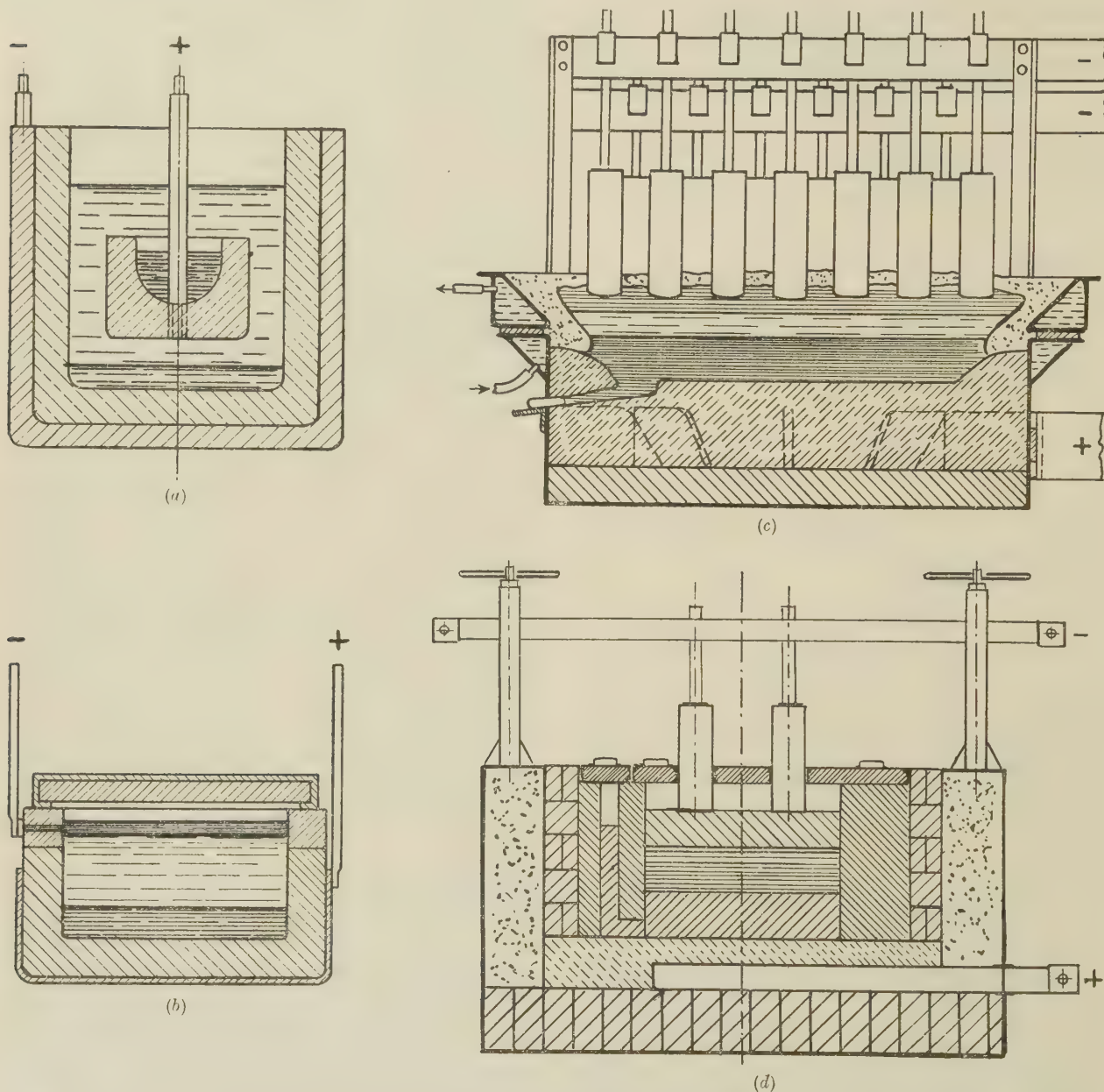


FIG. 7.—Electrolytic Cells for Refining Impure Aluminium. (a) Hoopes cell. (b) Betts cell. (c) Improved form of Hoopes cell developed by Frary and Edwards. (d) Cell developed by von Zeerleder for the process of Hulin, Gadeau, and Hurter.

cryolite bath at a temperature above the melting point of aluminium. He could not, however, overcome the difficulty of interference between the molten anode and cathode (Fig. 7 (a)). Betts, another of Hall's assistants, solved the problem in 1905, with his invention of three-layer electrolysis (Fig. 7 (b)). This

pure metal deposited at the cathode floats on the electrolyte. By these means crude aluminium can be refined to cathode metal of high purity. In spite of the low amount of electrochemical energy expended in this process, thermal losses in the 10,000–20,000-amp. cell bring the energy consumption up to 20

kWh./kg. of aluminium, which exceeds that of the ordinary Héroult-Hall reduction process. A process using an electrolyte of lower melting point has been developed by Hulin, Gadeau, and Hurter and is in industrial use for the production of metal of over 99.99% purity (see Table II and Fig. 7 (d)).

TABLE II.—*Electrolytes for Refining Aluminium.*

	ALCOA * (American)	A.F.C.† (French)	S.A.I.A.‡ (Swiss)
BaF ₂ , %	30-38	...	18
BaCl ₂ , %	...	60	...
NaF, %	25-30	17	18
CaF ₂ , %	16
AlF ₃ , %	30-38	23	48
Al ₂ O ₃ , %	0.5-5
Impurities, %	~2 (CuF ₂ + MgF ₂)
Melting point, °C.	900	750	700
Operating temp., °C.	950	800	750

* Aluminum Company of America.

† Cie. Alais, Froges et Camargue.

‡ S.A. pour l'Industrie de l'Aluminium.

Processes involving physical separation have been proposed as alternatives to these electrolytic treatments of silico-aluminium prepared by thermal reduction.

In the mercury process devised by Borchers and Schmidt, crushed ferro-silico-aluminium is leached with mercury at 600°-650° C. and 20-30 atm. pressure. Iron, silicon, titanium, and vanadium remain in the residue and can be filtered off. The solubility of aluminium in mercury decreases rapidly with fall of temperature, being 4% at 500° C. and 0.002% at 360° C. Complete separation of the mercury from the aluminium can be achieved by vacuum distillation. A very pure aluminium, practically free from mercury, can be obtained by this method, with ferro-silicon as a by-product. Mercury losses are said to be negligible. Messner has recently claimed that it is also possible to recover the whole of the aluminium combined with iron.

As long ago as 1883 Seymour proposed to extract the aluminium content from ferro-silico-aluminium with the aid of zinc, and in 1912 Viallay reported that the resulting aluminium-zinc alloy could be separated by distilling off the zinc. A similar process was developed for I.G. Farbenindustrie at Bitterfeld by Beck, but was abandoned in 1945. In that case the distillation was conducted in an induction furnace (Fig. 8). Further proposals for the industrial application of this process have recently been made by Foundaminsky and Loevenstein. An acceptable degree of purification results only if the aluminium content of the zinc does not exceed 10%. With a content of 20% the aluminium separated will contain as much as 0.5% iron. Complete recovery of aluminium from FeAl₃ cannot be expected with this method. It was also tried out by the Cie. Pechiney in France on a pilot-

plant scale for several years, but does not appear to have been translated on to a large industrial scale.

In all these extraction processes the silico-aluminium must be thoroughly crushed, as otherwise the leaching output will be low. Its composition has therefore to be controlled within narrow limits, to ensure satisfactory crushing without undue wear on the mill.

Another alternative, proposed by Kierseboom, consisted in the extraction of aluminium from sulphide or carbide with lead at 1200° C. At this temperature the solubility of aluminium in lead amounts to 1-1.5%, or even less when impure lead is used. On cooling to 650° C. the solubility falls to less than 0.1%. At this stage the aluminium is floating on the lead, but unfortunately it still contains 1-3% of lead which must be removed by alloying with magnesium or cadmium, or by vacuum distillation.

Fig. 9 illustrates the carbide (or sulphide) process. In the latter, lead sulphide is fed, together with bauxite,

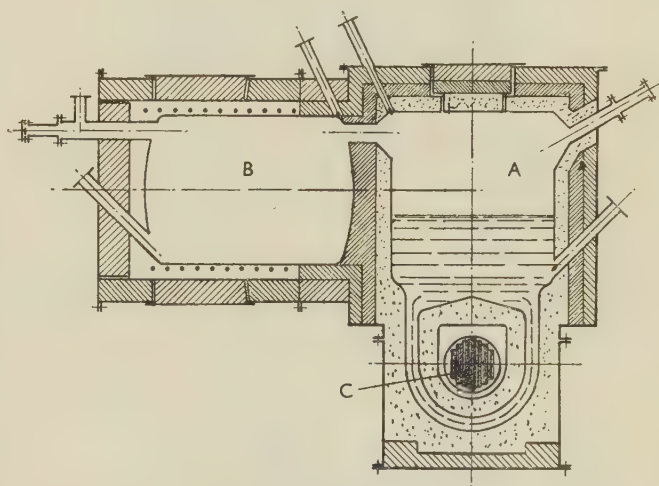


FIG. 8.—Diagram of the Beck-Schunk Low-Frequency Vacuum-Distillation Furnace.

KEY.

- A. Melting and distilling pot.
- B. Condenser with external heating.
- C. Electric induction heating.

coke, and pyrites into an electric furnace. The products are a lead-aluminium alloy, silicon- and titanium-bearing iron, and lead sulphide, which is recycled. The low-aluminium lead, taken from the separating furnace at 650° C., is also recycled. The drawbacks to the process consist in the difficulty of obtaining sufficiently pure aluminium sulphide (or carbide), and in the large quantity of lead—one hundred times the quantity of aluminium—that has to be handled and periodically purified. Provision must also be made to prevent loss of sulphur by oxidation and of lead by evaporation and oxidation.

A radically new possibility for the separation of aluminium from impure alloys springs from the discovery that aluminium at high temperatures may be monovalent. Baur and Brunner of the Eidgenössische Technische Hochschule were the first to recognize

aluminium suboxide; while Mitterbiller discovered in AlCl the first aluminium subhalide. He did not realize, however, that this subchloride is stable only at

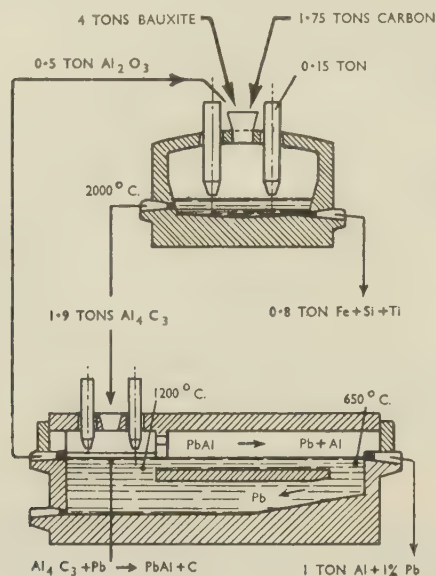


FIG. 9.—Sequence of Operations in the Kierseboom Process for the Extraction of Aluminium from its Sulphide or Carbide with Lead.

temperatures above 900° – 1000° C. and dissociates at lower temperatures into aluminium and AlCl_3 . Willmore has made use of fluorine for the separation of aluminium. Aluminium and a fluoride (e.g. cryolite) are milled, mixed, and compressed into briquettes.

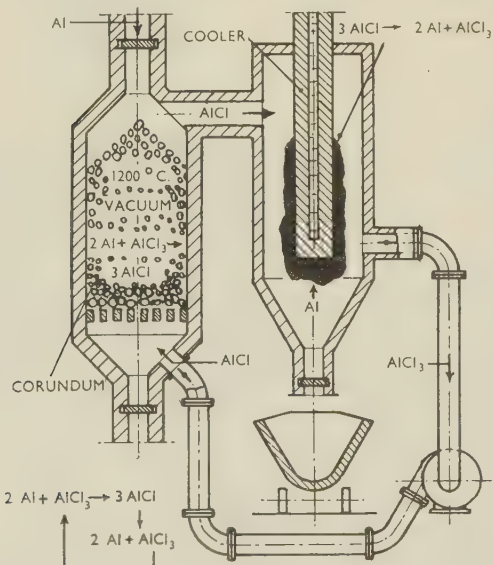


FIG. 10.—Sequence of Operations in the Moser Subhalide Distillation Process for the Production of Aluminium.

These are heated in a vacuum or in a hydrogen atmosphere to between 900° and 1300° C. Aluminium subfluoride distils off, and at 800° C. this dissociates to give aluminium and AlF_3 , which can be recycled.

Gross, at the Fulmer Research Institute, has worked with aluminium chloride. This can be evaporated and reacts with molten aluminium in a counter-current tower filled with ceramic material, at 1100° C. A similar technique has been developed by Moser at the Société Anonyme pour l'Industrie de l'Aluminium. An alternative procedure consists in bubbling chloride vapour through an aluminium melt in a kind of Bessemer converter. It also seems possible to combine the reduction and refining processes. For this purpose alumina must be made to react with carbon or silicon as a reducing medium, and with aluminium chloride vapour as a reactor, at a pressure of about 1 mm. Hg. Metallic aluminium is deposited on condensers at 600° C., while aluminium chloride is condensed on colder surfaces below 100° C. Aluminium chloride vapour can also be recycled directly, as shown in Fig. 10.

VI.—CONCLUSION

It is a striking fact that, apart from the Bayer method, only the Pedersen process has found any prolonged industrial application, and even that was under very special circumstances in Norway. During the war the technical aspects of the zinc-, magnesium-, and mercury-processes were developed by the important aluminium manufacturers, mainly for scrap-reclamation purposes, but none of them has been employed in any large-scale production since 1945.

The starting point of most of these processes is a silico-aluminium alloy, containing greater or lesser amounts of iron, similar to that used in the steel industry as a deoxidizer, but with a low enough iron content to make possible the separation of the aluminium from the silicon alloy. As already stated, such alloys contain at most 70% aluminium. If the iron content is to be kept low, they must be produced from kaolin and alumina, possibly with the addition of quartz. Suitable ores for the direct preparation of alloys containing between 60 and 70% aluminium do not occur naturally. The expense of separating such a crude alloy would be at least as high as the current price of pure aluminium. No provision can therefore be made for the additional costs of refining. The disposal of the silicon or ferro-silicon produced as a by-product will not go far towards solving the problem, since they are in a fragmentary and impure state and must undergo remelting, which involves additional expenditure. Every process so far tried for the production of aluminium of normal purity, for which a good demand exists, has proved unsuccessful on economic grounds. There is an increasing, though still rather limited, demand for high-purity metal, but although this commands a higher price, the processes available will not yield material of the purity required.

In conclusion, it would appear that the efforts to improve upon the methods of aluminium reduction in use for more than sixty years have not yielded one which can compete economically with the most modern version of the Héroult–Hall–Bayer process.

POROSITY AND PERMEABILITY CHANGES DURING THE SINTERING OF COPPER POWDER *

1600

By G. ARTHUR,† B.Sc., A.R.T.C.

SYNOPSIS

Porosity and permeability measurements have been made on copper powders sintered in hydrogen for periods up to 100 hr. at 1000° C. The effects of particle shape and size were investigated by using electrolytic (angular) and atomized (spherical) powders in the size ranges —240 + 300 and —300 mesh. By employing a method involving impregnation of the specimens with xylene, both the interconnected (ϵ_i) and the closed (ϵ_c) porosities were determined.

It was found that in both loose-sintered and precompacted specimens the porosity is mainly interconnected for most of the sintering process. During sintering the closed porosity (ca. 2%) remains practically constant, while the interconnected porosity decreases. It is therefore proposed that surface diffusion is possibly operative. At approximately 6% total porosity the interconnected porosity is zero and the closed porosity is a maximum.

The permeability, λ , of the loose-sintered specimens decreases with decreasing porosity but is still measurable at porosities of 10%. With cold-compacted specimens the permeability decreases with increasing compacting pressure. On sintering compacted specimens the permeability at first increases and then decreases with decreasing porosity.

By employing the Kozeny relationship :

$$S_0^2 = \frac{\epsilon_i^3}{(1 - \epsilon_i)^2 k \lambda}$$

values of the specific surface, S_0 , have been calculated from the experimental results. The variation of S_0 with ϵ_i is discussed and compared with values calculated from the model proposed by Clark and White (*Trans. Brit. Ceram. Soc.*, 1950, **49**, 305).

I.—INTRODUCTION

THE conception of sweat-cooling gas-turbine blades has caused considerable attention to be directed towards the production of metal bodies permeable to gases and liquids. Sweat-cooling consists of forcing the coolant fluid through pores in the material to the heat-exposed surface. Cooling takes place first, by conduction, as the fluid passes through the pores, and secondly, by the formation of a heat-insulating layer at the surface of the component.

Powder-metallurgy techniques offer a convenient method for the production of bodies with small evenly distributed pores, such as are required in this case, and various investigators have studied the problem of making porous metals having a controlled permeability.

Duwez and Martens¹ found that no relationship existed between the porosity and permeability of pressed and sintered nickel-molybdenum-iron specimens. However, by making additions, before pressing, of ammonium bicarbonate, which volatilized during sintering, relationships were obtained on the one hand between the percentage of ammonium bicarbonate added and the porosity, and on the other between the porosity and the permeability.

Grootenhuis and Moore² in an investigation of the permeability of copper-tin specimens found a linear

relationship between the logarithms of the permeability and the porosity, even though the particle sizes were not the same in each specimen.

The pores in a sintered specimen can be divided into two categories : (i) pores connected to the surface of the specimen, called here the interconnected pores, and (ii) closed pores bounded on all sides by solid material. Closed pores, obviously, do not contribute to permeability, and if any relationship exists it would be expected to be between the permeability and the interconnected porosity, not the total porosity. The main aim of the present work has been to investigate how the relative proportions of closed and interconnected pores vary during sintering and to study the relationship, if any, between permeability and interconnected porosity.

II.—THEORETICAL CONSIDERATIONS

The nature of gas flow through a porous body, which can be regarded as a system of small pipes, may be one of three types. At high gas pressures and velocities the flow is completely turbulent, and at any point the pressure and velocity fluctuate about the mean values. As the pressure and velocity are decreased, the nature of the flow changes. The lines of flow become regular, being either straight or gently curved. As the viscosity of the gas is a major factor in deciding the amount of flow, this type is known as

* Manuscript received 11 August 1954.

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"viscous flow". When the pressure of the gas is so low that the mean free path of the molecules becomes of the same order as the diameter of the tube or pore, the gas flow becomes diffusional in character. The viscosity of the gas is no longer important, as gas molecules collide with the walls of the tube rather than with each other. This is normally known as "molecular flow".

In the present work only the viscous-flow range has been investigated, in which the permeability is defined by the equation first derived by D'Arcy³:

$$\frac{Q}{\frac{A}{p_2^2 - p_1^2}} = \lambda \frac{\rho_1}{2p_1 u}$$

where Q = weight rate of flow, A = cross-section over which flow is taking place, L = thickness of specimen, p_2 = pressure on entry side, p_1 = pressure on exit side, ρ_1 = density of gas at p_1 , u = viscosity of gas, and λ = permeability coefficient.

$$\text{As } Q = \frac{p_1 v_1 M}{RT} \text{ and } \rho_1 = \frac{p_1 M}{RT},$$

the equation reduces to:

$$v_1 = \lambda(p_2 - p_1) \frac{(p_2 + p_1)}{2p_1} \frac{A}{Lu}$$

and making $\frac{p_2 + p_1}{2} = p$, the mean pressure across the specimen, we have:

$$\frac{p_1 v_1}{p} = \lambda \Delta p \frac{A}{Lu}$$

where

$$\Delta p = p_2 - p_1.$$

In the present case the volume of the gas flowing was measured at atmospheric pressure, and denoting this pressure and the corresponding volume by p_0 and v_0 , respectively, we can write:

$$\frac{p_0 v_0}{p} = \lambda \Delta p \frac{A}{Lu} \quad (p_0 v_0 = p_1 v_1)$$

The gradient of a plot of $\frac{p_0 v_0}{p}$ against Δp , the pressure difference across the specimen, thus gives $\lambda \frac{A}{Lu}$, and knowing the viscosity of the permeating gas and measuring A and L , the permeability coefficient can be obtained. This permeability coefficient, which has the dimensions L^2 , is thus independent of the dimensions of the specimen and the nature of the permeating fluid.

It has been shown theoretically by Kozeny⁴ and experimentally by several investigators^{5, 6} that the permeability coefficient is related to the porosity and specific surface of the specimen by the equation:

$$\lambda = \frac{\epsilon^3}{(1 - \epsilon)^2 k S_0^2}$$

where ϵ is the fractional porosity, S_0 is the specific surface in $\text{cm}^2/\text{c.c.}$ of solid material, and k , Kozeny's constant, is a dimensionless constant. This constant was shown by Kozeny to be equal to 5 for spherical material, and Carman⁵ has established that only small deviations from this figure may be expected for non-spherical materials. Thus, by measuring the permeability and porosity of the specimen, values of the specific surface can be calculated.

III.—EXPERIMENTAL PROCEDURE

Experiments were made on loose-sintered and on precompacted copper powder. In the loose-sintering experiments both atomized and electrolytic powders were used in the size ranges $-240 +300$ mesh and -300 mesh, so that the effect of particle shape and size on the quantities measured could be determined. The density of the powders was found, by the density-bottle method, to be 8.90 in each case.

Sintering was carried out in a Kanthal-wound horizontal furnace, the heating chamber of which was a silica tube. The furnace atmosphere in all cases was hydrogen. The temperature, measured by a platinum/platinum-rhodium thermocouple, was controlled within $\pm 2^\circ \text{C.}$ by means of a Kelvin-Hughes electronic controller.

Accurate permeability measurements require that at least two faces of the specimen be closely parallel and for this reason, in the loose-sintering experiments, the powder was placed in a cylindrical alumina crucible into which was inserted another, smaller, but tightly fitting crucible. The powder was thus contained between two parallel alumina faces and could not be disturbed on being inserted into the furnace. This procedure was dispensed with when the particles had bonded together after the initial sintering.

Experiments in which the powder was precompacted were confined to the $-240 +300$ mesh electrolytic powder; it proved impossible to cold press the atomized material. Specimens were pressed at 5, 10, 15, 20, and 30 tons/in.² and subsequently sintered for various times at 1000°C.

1. MEASUREMENT OF PERMEABILITY

As explained above, in order to determine the permeability coefficient it is necessary to know the quantity of fluid flowing through the specimen for a given pressure drop. The gas used in the present case was nitrogen, which has a viscosity of 174×10^{-6} poises at 20°C. The volume flowing was measured by means of an orifice-type flow-meter containing butyl phthalate, and the pressure difference by a manometer also containing butyl phthalate. At lower permeabilities this manometer was replaced by one containing mercury, so that larger pressure differences could be measured.

So that gas flow should take place over a known

cross-sectional area, the specimen holder shown in Fig. 1, was designed. The specimen was placed between two brass flanges held together by six bolts.

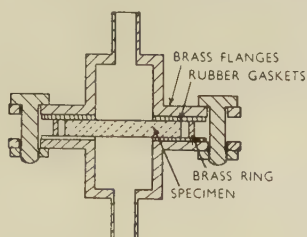


FIG. 1.—The Specimen Holder.

Rubber gaskets and a brass ring of approximately the same height as the specimen prevented leakage of gas from the sides and edges of the specimen, respectively. Gas flow occurred over a circle $\frac{3}{4}$ in. in dia., giving a value of A of 2.84 cm.².

2. MEASUREMENT OF POROSITY

The specimens, immersed in xylene, were placed in a vacuum desiccator and the pressure reduced to approximately 10 μ Hg for a period of 20 min. This treatment removed gas from the open pores and allowed the xylene to enter. The specimens were then removed from the xylene, and after the surface liquid had been wiped off by means of filter paper, they were weighed in air and in water. The xylene, being non-miscible with water, prevented the water from entering the pores, so that the difference between the last two weighings gave the total volume of the specimen.

Letting A_1 = weight of specimen, B = weight of specimen after impregnation with xylene, and C = weight of impregnated specimen in water:

$$B - C = \text{volume of specimen}$$

$$\epsilon_i = \frac{(B - A_1)}{(B - C)\rho_x} \quad \text{and} \quad \epsilon = \frac{(B - C) - \frac{A_1}{\rho_{Cu}}}{(B - C)},$$

where ϵ_i and ϵ are the interconnected and total porosities, respectively, and ρ_x and ρ_{Cu} are the densities of xylene and copper. The difference between ϵ and ϵ_i gives ϵ_c , the closed porosity. Results obtained by this method were in good agreement with those reached by the more conventional method, in which the specimen is plunged into boiling water to fill the pores and then, after weighing and drying, coated with wax and weighed in air and water to determine the volume.

IV.—EXPERIMENTAL RESULTS

1. PERMEABILITY

The relationship between permeability and interconnected porosity for -240 +300 mesh atomized copper powder, loose-sintered at 1000° C. for periods up to 100 hr., is illustrated in Fig. 2. Curves of

similar shape were obtained for the other powders studied.

In Fig. 3 is shown a plot of $\log \lambda$ against $\log \frac{\epsilon_i^3}{(1 - \epsilon_i)^2}$.

Provided that S_0 , the specific surface, is constant, such a plot should give a straight line of slope 1. This is obviously not the case. At high porosities little difference exists between the permeabilities, for a

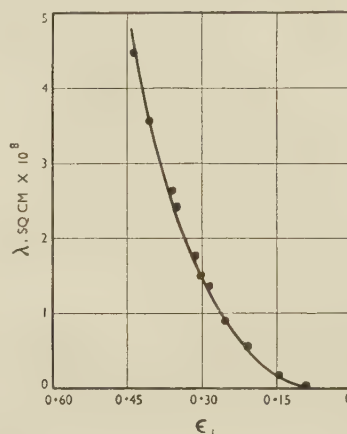


FIG. 2.—Variation of Permeability (λ) with Interconnected Porosity (ϵ_i) for -240 + 300 Mesh Atomized Copper Powder.

given porosity, of the atomized and electrolytic powders in the same size range. At lower porosities the curves for the -300 mesh copper powders diverge; for a given porosity the electrolytic powder has a lower permeability than the atomized. The size

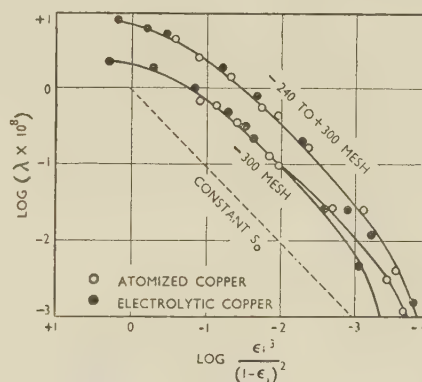


FIG. 3.—Log Permeability Plotted Against $\log \frac{\epsilon_i^3}{(1 - \epsilon_i)^2}$.

analyses for the -300 mesh powders, as determined on a Heywood-type sedimentometer, are shown in Table I.

TABLE I.—Size Analyses of -300 Mesh Copper Powders.

-300 Mesh Copper Powder	45-35 μ	35-25 μ	25-15 μ	15-5 μ	-5 μ
Electrolytic	38%	37%	23%	2%	0
Atomized	25%	38%	27%	10%	0

Fig. 4 gives the results of the experiments on the cold-pressed and sintered specimens. With increase in compacting pressure from 5 to 30 tons/in.², the

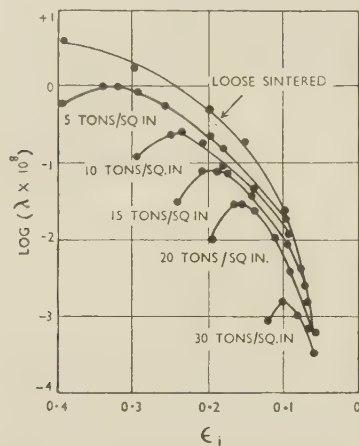


FIG. 4.—Variation of Permeability with Interconnected Porosity of Electrolytic Copper Powder, Loose-Sintered or Pre-compacted at Pressures Shown. Specimens cold pressed and subsequently sintered for various times at 1000° C.

permeability and the interconnected porosity decrease. On sintering, the permeability in each case at first increases even though the interconnected porosity is decreasing. Further sintering causes the permeability to decrease with decreasing porosity until in each case values are reached similar to those for the uncompacted powder.

2. POROSITY

In Fig. 5 are shown the interconnected and closed porosities plotted against the total porosity for the

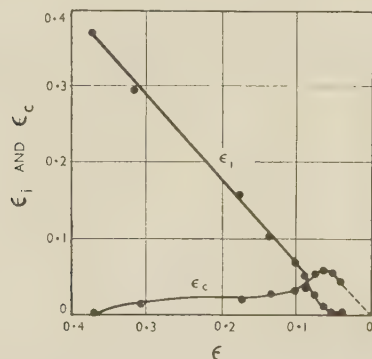


FIG. 5.—Variation of Interconnected (ϵ_i) and Closed (ϵ_c) Porosities with Total Porosity (ϵ) for -300 Mesh Atomized Copper Powder.

-300 mesh atomized powder loose-sintered at 1000° C. Similar results were obtained with the other three powders when loose-sintered, although in both the size ranges the percentage of open pores in the earlier stages of sintering was slightly greater for the electrolytic than for the atomized powder. The figure illustrates the fact that during most of the sintering process the closed pores form only a small

percentage of the total porosity. At approximately 9% porosity the two types of pore are present in equal amounts; thereafter the closed pores rise to a maximum of about 6% and then decrease.

Similar results for the cold-pressed and sintered electrolytic powder are shown in Fig. 6. The line drawn through the points for open and closed pores is that obtained with uncompacted powder.

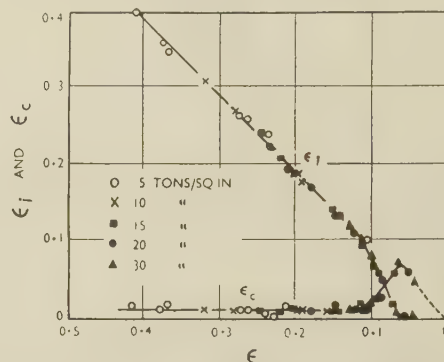


FIG. 6.—Variation of Interconnected and Closed Porosities with Total Porosity for -240 + 300 Mesh Electrolytic Copper Powder, Cold Compacted at Pressures Shown.

Obviously, compacting pressures up to 30 tons/in.² do not influence the amount of open and closed pores at a given porosity.

V.—DISCUSSION OF RESULTS

1. VARIATION OF SPECIFIC SURFACE

(a) Uncompacted Powder

Using the Kozeny equation, values of S_0 , the specific surface in cm.²/c.c. of solid material, have been calculated at various porosities during sintering, and are plotted against the interconnected porosity in Fig. 7. The terminal point of the lines at the high-porosity end is, in each case, the specific surface obtained on the uncompacted unsintered powder. The specific-surface values are given in Table II, together

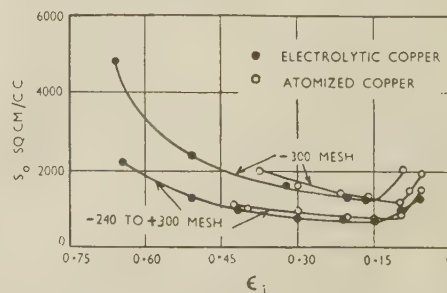


FIG. 7.—Variation of Specific Surface (S_0) with Interconnected Porosity.

with the tap porosities, i.e. the porosities of the powders after they had been brought to a constant volume by tapping in a measuring cylinder.

In the case of the $-240 + 300$ mesh atomized powder, a value of $1040 \text{ cm.}^2/\text{c.c.}$ was obtained for the specific surface. The aperture sizes on 240 and 300

TABLE II.—Specific Surfaces and Tap Porosities for Copper Powders.

Size Fraction	Electrolytic		Atomized	
	S_0	ϵ	S_0	ϵ
$-240 + 300$	2200	0.66	1040	0.43
-300	4860	0.64	2000	0.37

mesh screens are 66 and 47μ , respectively. Assuming a linear distribution between these two sizes, the mean particle diameter can be taken as 56μ . As the particles are spheres,

$$S_0 = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r} = \frac{6}{d} = \frac{6}{56 \times 10^{-4}} = 1070 \text{ cm.}^2/\text{c.c.},$$

showing that the permeability method gives fairly accurate results, at least in the case of spheres.

In each case the specific surface at first decreases on sintering, and this may be regarded as being the effect of bonding between particles.

The values of the specific surface for both the electrolytic powders drop very rapidly in the early stages of sintering, and this is considered to be due to a reduction in angularity of the powder. A noteworthy feature of the results is that by the time the electrolytic specimens have been sintered to the tap density of the atomized powder in the same size range, the specific surface is approximately the same as that of the atomized powder. With further decrease in porosity the specific surfaces of the atomized and electrolytic specimens continue to be approximately the same, although in both cases the values for the electrolytic specimens are slightly lower. This similarity in the specific surfaces is considered to indicate that a parallel similarity exists in the pore structure of the two specimens, i.e. when the electrolytic specimens have been sintered to the density of the atomized powder in the same size range, the flow of material has been such as to remove most of the additional angularity of the former powder.

At lower porosities the specific surface starts to increase again in each case, and this, it is thought, can be explained in the following way. Open pores can be divided into two categories: (i) those connected to one surface of the specimen only, and (ii) those with connections to two opposite sides of the specimen. Only the latter porosity should be inserted in the Kozeny relationship when calculating the specific surface, so that by using ϵ , a measure of both types of open pores, an over-estimated value of the specific surface is obtained. This error is probably small in the early stages of sintering, but at higher densities when the open porosity is smaller the fraction of blocked pores must increase, causing a larger error in the calculated specific surface.

(b) Calculation of the Variation in S_0 with ϵ , Using the Model of Clark and White⁷

Clark and White⁷ proposed a theory based on the model shown in Fig. 8, in which they calculated the rate of shrinkage in the initial or open-pore stage of sintering. As this is the stage investigated in the present work, their model has been used to calculate how S_0 , the specific surface, varies with ϵ , the porosity.

Clark and White assume that the particles remain spherical during sintering but decrease in volume;

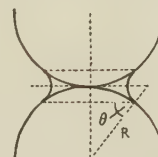


Fig. 8.—Clark and White's Model, Showing Caps of Spheres Covered by a Lens.⁷

the material resulting from this change in volume forms the lenses between the particles. From this assumption it follows that:

$$\frac{\text{Initial bulk volume}}{\text{Final bulk volume}} = \frac{\text{Initial sphere volume}}{\text{Final sphere volume}} = \left(\frac{R_0}{R}\right)^3 \quad (1)$$

where R_0 and R are the initial and final sphere radii. Thus, values of ϵ can be calculated for varying values of R when R_0 is known. To calculate the specific surface, the surface area per unit volume of material must be found. Taking as the unit the material associated with one particle we have:

$$\text{Volume} = \text{volume of particle} + \frac{n}{2} (\text{volume of a lens})$$

where n is the number of points of contact per particle. Clark and White have shown that the volume of a lens

$$= A_2 R^3$$

$$\text{where } A_2 = 2\pi \left\{ \frac{1-x}{x} \right\}^2 \left\{ 1 - \frac{\theta \sqrt{1-x^2}}{x} \right\} \quad (2)$$

and $x = \sin \theta$ (Fig. 8).

Thus the volume of material per particle

$$= \frac{4}{3}\pi R^3 + \frac{n}{2} A_2 R^3 \quad (3)$$

The surface area per particle

$$\begin{aligned} &= (\text{Surface of sphere} - n \text{ caps}) + \frac{n}{2} (\text{Surface of lens}). \\ &= \{4\pi R^2 - n2\pi R^2(1-x)\} \\ &\quad + \frac{n}{2} \left\{ 4\pi R^2 \theta \left(\frac{1-x}{x} \right)^2 \left(\frac{\sqrt{1-x^2}}{1-x} - 1 \right) \right\} \\ &= 2\pi R^2 \left\{ 2 - n(1-x) + n\theta \left(\frac{1-x}{x} \right)^2 \left(\frac{\sqrt{1-x^2}}{1-x} - 1 \right) \right\} \quad (4) \end{aligned}$$

The specific surface is then given by :

$$S_0 = \frac{2\pi R^2 \left\{ 2 - n(1-x) + n\theta \left(\frac{1-x}{x} \right)^2 \left(\frac{\sqrt{1-x^2}}{1-x} - 1 \right) \right\}}{2\pi R^3 \left\{ \frac{2}{3} + \frac{nA_2}{4\pi} \right\}} = \frac{2 - n(1-x) + n\theta \left(\frac{1-x}{x} \right)^2 \left(\frac{\sqrt{1-x^2}}{1-x} - 1 \right)}{R \left(\frac{2}{3} + \frac{nA_2}{4\pi} \right)} \quad (5)$$

As the initial porosity of the $-240 + 300$ mesh atomized powder was 0.43, the value of n can be taken as approximately 7. A can then be calculated for various values of R from the relationship deduced by Clark and White.

$$nA_2 = 8.35 \left\{ \left(\frac{R_0}{R} \right)^3 - 1 \right\} \quad (6)$$

and by solving equation (2) graphically, values of x and θ are obtained.

The solution of equations (1) and (5) for various values of R then gives the relationship between S_0 , the specific surface in $\text{cm}^2/\text{c.c.}$, and ϵ , the porosity. These equations were solved in the case of the $-240 + 300$ mesh atomized copper powder where the necessary conditions were approximately fulfilled, i.e. evenly sized spherical particles. The relationship obtained is shown in Fig. 9, together with that found

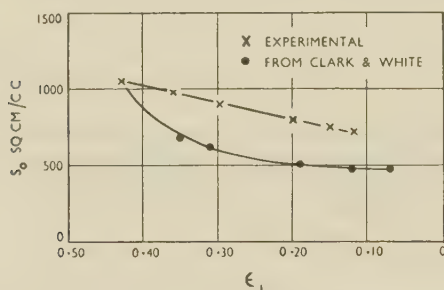


FIG. 9.—Variation of Specific Surface with Interconnected Porosity for $-240 + 300$ Atomized Copper Powder.

experimentally. The values obtained using Clark and White's model are considerably lower than those determined experimentally, suggesting that the model does not accurately represent the sintering process. Confirmation of this is obtained from the porosity results. Thus, for a value of $n = 7$ it can be shown⁷ that merging of the lenses begins when $\sin \theta$ is approximately 0.75. Using equations (2), (6), and (1), this value of $\sin \theta$ corresponds to a value of ϵ of 33%, i.e. at 33% porosity all the pores should be closed. It has been found experimentally, however (Figs. 5 and 6), that at 33% porosity the closed pores represent only approximately 5% of the total porosity.

(c) Effect of Cold Pressing

In Fig. 10 are shown values of the specific surface calculated for each of the five cold-pressed specimens. The increase in specific surface with rise in compacting pressure is considered to be due to the increasing deformation of the particles and the exposure, by slip, of new surfaces. On sintering for 15 min. at 1000°C. (second points on curves in Fig. 10), the

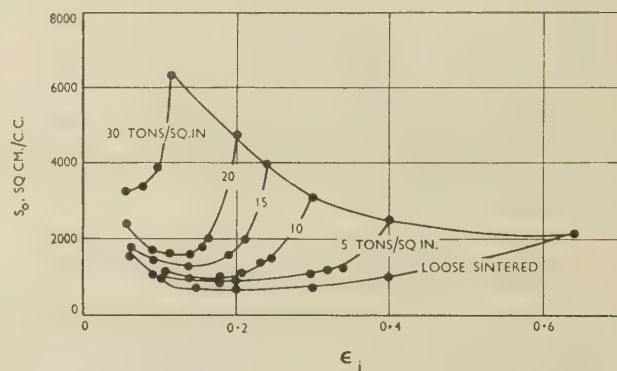


FIG. 10.—Variation of Specific Surface with Interconnected Porosity for Electrolytic Copper Powder, Loose-Sintered or Precompactd at Pressures Shown.

specific surface in each case undergoes a large decrease, probably due to the levelling out of slip steps by a process of surface diffusion. It is this large decrease in specific surface which is responsible for the initial increase in permeability obtained on sintering these cold-pressed specimens. The graph of specific surface against porosity for the uncompacted electrolytic powder is also shown in Fig. 10. Only at low porosities (i.e. < 0.1), where the specific-surface values are in any case uncertain, do the curves converge. At higher porosities the values for the compacted powder are, in each case, greater than for the uncompacted powder, indicating that part of the results of the original deformation persists during sintering.

Thus, precompacting of metal powders, in addition to decreasing the initial porosity, causes an increase in the specific surface which, being the driving force behind sintering, results in faster rates of sintering.

2. VARIATION IN CLOSED AND INTERCONNECTED POROSITY

The fact that closed pores remain practically constant for most of the sintering time, while the open pores decrease, may be explained by one of two processes :

(a) Closed pores are being formed from open pores and being removed at approximately the same rate, so that at any given time the amount of closed pores is constant.

(b) The increase in density during sintering is due to the reduction in volume of the open pores.

Most probably the two processes are taking place simultaneously to a greater or lesser extent, i.e. both closed and open pores are shrinking and some closed pores are being formed from open pores. At high densities ($\epsilon = < 0.1$), the rate at which closed pores are forming from open pores exceeds the rate of shrinkage of closed pores, so that the latter increase until the open porosity has been eliminated.

It has been generally supposed^{8,9} that during sintering closed pores predominate, and most of the sintering theories have been based on this assumption. These theories have therefore necessarily been based on mechanisms by which material could be transported between pores separated by solid copper. Thus, MacKenzie and Shuttleworth's theory⁸ depends on a model in which spherical pores are surrounded by material which can undergo either viscous or plastic flow under the applied stress of surface tension. On the other hand, Rhines, Birchenall, and Hughes⁹ consider that a diffusion mechanism is operative, in which vacancies migrate from the regions of high concentration in the neighbourhood of pores to the surface of the specimen.

None of the theories explains all the experimental facts. The curves of density against time of MacKenzie and Shuttleworth⁸ fit the observed curves in the later but not in the earlier and more rapid stages of sintering,¹⁰ whereas the diffusional theory predicts rates of sintering which are too low.⁸ This latter theory also requires that pores near the surface of the specimen should close more rapidly than those in the interior. In the present work, however, it has been found that pores connected to the surface persist for the greater part of the sintering process. It has been pointed out that mosaic and grain boundaries may act as sinks for vacancies,^{11,12} and this would lead to sintering rates higher than those calculated by Rhines, Birchenall, and Hughes. Assuming that such a mechanism is operative, pores near the surface of the specimen would still be expected to close more rapidly than others.

The fact that most of the pores are surface-connected during the major portion of the sintering time means, however, that it is unnecessary for material to move between pores separated by solid metal, and that it is possible for surface diffusion to be operative. It is generally considered that surface diffusion is much more rapid than volume diffusion, and Kuczynski,¹³ in experiments on copper has shown that the ratio of D_0 for surface diffusion is approximately 10^5 times that for volume diffusion. Confirmation of this figure is provided by the work of Winegard and Chalmers,¹⁴ who also obtained a value of 10^5 for this ratio in the case of the similar metal, silver. Thus, an analysis of sintering rates, bearing in mind that surface diffusion could be operative, would yield results higher than those of Rhines, Birchenall, and Hughes and probably be in better agreement with those of experiment.

VI.—CONCLUSIONS

(1) During the loose-sintering of copper powder in hydrogen, the permeability decreases with decreasing porosity. On sintering cold-compacted specimens, the permeability first increases then decreases with decreasing porosity. In all cases there is still a measurable permeability at densities equal to 90% of theoretical.

(2) The specific surface of the loose-sintered specimens, calculated from the Kozeny relationship, decreases during the earlier stages of sintering. An increase at higher densities is thought to be due to an over-estimated value of ϵ_i . S_0 increases with increasing compacting pressure and thus cold compacting, as well as increasing the initial density, provides the additional driving force necessary for faster rates of sintering. The sintering of cold-compacted specimens results in a rapid decrease in S_0 , probably due to the levelling of slip steps by a process of surface diffusion.

(3) After the initial sintering period, values of the specific surface for the two types of powders in each of the size ranges are similar, indicating that the additional angularity of the electrolytic powder is removed in the early stages of sintering. Similarly, most, although not all, of the deformation caused by cold pressing is rapidly removed by sintering.

(4) During most of the sintering process porosity connected to the surface of the specimen predominates over closed porosity. The proportion of open to closed pores is not influenced by cold compacting with pressures up to 30 tons/in.².

(5) As a consequence of the result recorded in (4) criticisms can be made of the current sintering theories. For example, by using the model of Clark and White,⁷ it can be shown that in the case of $-240 + 300$ mesh atomized copper powder the pores should be completely closed when the porosity is 33%. This prediction is at variance with the experimental facts. A similar objection can be raised against the model on which the theory of MacKenzie and Shuttleworth⁸ is based. The diffusion theory of Rhines, Birchenall, and Hughes⁹ predicts that pores near the surface should close before those in the interior of the specimen, but in the present work this has not been found to be the case.

On account of the existence of pores connected to the surface of the specimen, it is proposed that surface diffusion is possibly operative during sintering.

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REFERENCES

1. P. Duwez and H. E. Martens, *Trans. Amer. Inst. Min. Met. Eng.*, 1948, **175**, 848.
2. P. Grootenhuis and N. P. W. Moore, *Iron Steel Inst. Special Rep.*, 1952, (**43**), 281.
3. See e.g. M. Muskat, "The Flow of Homogeneous Fluids Through Porous Media". 1937: New York (McGraw-Hill Book Co.).
4. J. Kozeny, *Sitzber. Akad. Wiss. Wien*, 1927, [IIa], **136**, 271.
5. P. C. Carman, *Trans. Inst. Chem. Eng.*, 1937, **15**, 150.
6. F. M. Lea and R. W. Nurse, *J. Soc. Chem. Ind.*, 1939, **58**, 277.
7. P. W. Clark and J. White, *Trans. Brit. Ceram. Soc.*, 1950, **49**, 305.
8. J. K. MacKenzie and R. Shuttleworth, *Proc. Phys. Soc.*, 1949, [B], **62**, 833.
9. F. N. Rhines, C. E. Birchenall, and L. A. Hughes, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, **188**, 378.
10. P. W. Clark, J. H. Cannon, and J. White, *Trans. Brit. Ceram. Soc.*, 1953, **52**, 1.
11. A. D. Smigelskas and E. O. Kirkendall, *Trans. Amer. Inst. Min. Met. Eng.*, 1947, **171**, 130.
12. L. C. C. da Silva and R. F. Mehl, *ibid.*, 1951, **191**, 155.
13. G. C. Kuczynski, *ibid.*, 1949, **185**, 169.
14. W. C. Winegard and B. Chalmers, *Canad. J. Physics*, 1952, **30**, 422.

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SYNOPSIS

Aluminium-copper-cadmium alloys showed outstanding hot workability when rolled to sheet on a semi-industrial scale. Only negligible age-hardening occurred at room temperature, but an artificially aged uncoated alloy with 5% copper and 0.14% cadmium gave values of 25 tons/in.² for the 0.1% proof stress and 30 tons/in.² for the maximum stress in both the transverse and longitudinal directions. Cold working before artificial ageing markedly raised the tensile properties of aluminium-copper alloys, but reduced the properties of the aluminium-copper-cadmium alloys. The proof stress might drop by as much as 3 tons/in.², but the effect was greatly minimized by a short pre-ageing treatment at 165° or 170° C. before cold rolling. The fall in strength could also be minimized if the solution-treated and cold-worked sheet received a "stress-relief" treatment of 2 min. in oil at 200°–210° C.

Fully aged aluminium-copper-cadmium sheet alloys were immune from stress-corrosion and displayed intracrystalline attack when sprayed with 3% sodium chloride solution. Stress-corrosion occurred in these alloys when aged for 3 hr. at 170° C. An aluminium-copper alloy containing no cadmium showed inferior resistance even when aged to its peak (40 hr.) at 165° C. Both the cadmium-free and cadmium-containing sheet materials were highly resistant when cold worked and aged to give peak properties.

I.—INTRODUCTION

It has recently been shown that small quantities of cadmium, indium, or tin exert a pronounced influence on the response to artificial ageing of aluminium-copper alloys. The rate of artificial ageing is greatly enhanced,¹ and the strength properties, notably the proof stress, are increased to values unattainable in the absence of these elements.² Cadmium is the most suitable addition for practical applications, since its action is not inhibited by small quantities of magnesium, and also because undissolved cadmium does not affect the ductility of the alloy at room temperature.

Aluminium-copper-cadmium alloys have been successfully hot forged on an experimental scale.³ An attempt to produce uncoated sheet under normal industrial conditions met with immediate success, and these materials have been used to make a survey of the properties of technical interest. The present paper covers investigations of the solution-treatment conditions, the room- and elevated-temperature ageing characteristics, the effect of cold-work before artificial ageing, the annealing behaviour, and the stress-corrosion properties. A limited amount of comparative work has also been carried out on cadmium-free aluminium-copper alloys. Although only single values are quoted in the graphs and tables of tensile values, these are always averaged results from two or more tests.

The general development of aluminium-copper-cadmium alloys has been described elsewhere.⁴

II.—PRODUCTION OF SHEET

Rolling billets were prepared by the semi-continuous casting process,⁵ and their melt analyses are given in Table I. The rolling schedules are set out in Table II.

The alloys with about 4½% copper (ref. *FY* and *FZ*) were hot rolled at 455° C. to 0.25 in. thick. The

TABLE I.—Chemical Analyses of Al-Cu and Al-Cu-Cd Alloys.

Alloy Ref.	Cu, %	Mg, %	Si, %	Fe, %	Mn, %	Ti, %	Cd, %
<i>FY</i>	4.37	<0.02	0.21	0.16	0.58	0.04	Nil
<i>FZ</i>	4.27	<0.02	0.23	0.20	0.59	0.07	0.097
<i>GJ, GL</i>	5.0	<0.02	0.09	0.15	0.47	<0.02	0.14

TABLE II.—Rolling Schedules for Sheet Materials.

	<i>FY</i> and <i>FZ</i>	<i>GJ</i> and <i>GL</i>
Size of scalped billet	5 × 18½ × 10½ in. (<i>FY</i>) 5 × 18½ × 14 in. (<i>FZ</i>)	4½ in. × 13½ × 30½ in.
Preheating treatment	12 hr. at 480° C.	8 hr. at 480° C.
Rolling temperature	455° C.	480° C.
Dimensions of rolled slab	0.25 in. × 30 in. wide	0.25 in. × 41 in. wide
Intermediate anneals : 30 min. at 360° C. at	0.25 in. 0.11 in. 0.070 in.	0.25 in. 0.080 in., 0.080 in. 0.055 in.
Final gauge	0.048 in.	0.036 in.
Heat-treatment	Laboratory	Laboratory (<i>GJ</i>) Production (<i>GL</i>)

cadmium-free alloy (*FY*) rolled excellently and showed only negligible edge cracking. The alloy containing cadmium also rolled quite well, but gave slight edge cracking, ¼ to ½ in. deep.

The second batch of material, with higher copper (5%) and cadmium (0.14%) contents (ref. *GJ* and *GL*), showed outstanding hot workability when rolled at 480° C. Although a minimum number of passes was used, no trace of edge cracking was observed.

Cold rolling to final gauge followed a normal course.

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Materials *FY*, *FZ*, and *GJ* were subsequently heat-treated in the laboratory, but sheets $96 \times 48 \times 0.036$ in. of material *GL* were heat-treated on a production scale for 30 min. at 530°C . in a salt-bath, cold-water quenched, roller-levelled, and stretched to flatten them.

High-temperature tensile tests have been carried out on specimens taken from a cast billet.⁴ Over the range $440^\circ\text{--}530^\circ\text{C}$., the maximum stress fell continuously from about $2\frac{1}{2}$ to 1 ton/in.², whilst the elongation increased continuously from 55 to 95%. Consequently it might be possible to employ a rolling temperature even higher than 480°C . and so reduce the number of passes still further.

III.—SURVEY OF PROPERTIES

1. RESPONSE TO HEAT-TREATMENT

(a) Effect of Different Solution-Treatment Conditions (Tables III and IV)

The tensile-test results obtained on the solution-treated and artificially aged alloys containing $4\frac{1}{4}\%$

TABLE III.—Averaged Transverse Tensile-Test Results on $\text{Al-}4\frac{1}{4}\%$ Cu Sheet Alloys (*FY* and *FZ*) Solution-Treated in a Circulating-Air Furnace and Aged as Indicated.

Alloy Ref.	Temp., $^\circ\text{C}$.	Time	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	El., %
<i>FY</i> $\text{Al-}4\frac{1}{4}\%$ Cu	Aged for 16 hr. at 165°C .				
	530	10 min.	13.9	22.3	16
	530	30 "	14.3	23.7	$14\frac{1}{2}$
	530	1 hr.	15.3	25.2	14
	530	4 "	16.2	25.3	13
	Aged for 6 hr. at 185°C .				
	520	30 min.	8.2	19.1	16
	530	"	9.8	20.0	15
	540	"	10.4	20.4	15
	Aged for 16 hr. at 165°C .				
<i>FZ</i> $\text{Al-}4\frac{1}{4}\%$ Cu-0.1% Cd	530	10 min.	23.3	28.4	10
	530	30 "	23.0	28.4	$10\frac{1}{2}$
	530	1 hr.	24.0	28.9	$10\frac{1}{2}$
	530	4 "	24.2	28.9	$8\frac{1}{2}$
	Aged for 6 hr. at 185°C .				
	520	30 min.	21.6	26.8	10
	530	"	22.3	27.8	10
	540	"	23.2	28.6	$10\frac{1}{2}$

copper (*FY* and *FZ*) are given in Table III. A very clear distinction is apparent between the cadmium-free and cadmium-containing materials. For the aluminium-5% copper-0.14% cadmium alloys (Table IV) only a negligible difference existed between the properties in the transverse and longitudinal directions. The salt-bath and air-furnace heat-treatments produced very similar results. Progressively lower tensile values were encountered when the heat-treatment temperature was reduced from 530° to 490°C . A solution-treatment of 30 min. at 530°C . in a circulating-air furnace was chosen as the standard procedure for the remainder of the work.

It had been noted earlier that loss of cadmium occurred from the surface during salt-bath heat-treatment of very high-purity alloys.¹ Spectrographic analysis failed to detect a similar effect in the case of the alloys of commercial purity now being examined, which had been solution-treated either in an air furnace or in a salt-bath.

(b) Ageing at Room Temperature (Tables V and VI)

Ageing at room temperature was very slow. The alloys with $4\frac{1}{4}\%$ copper (*FY* and *FZ*) gave proof-stress values of about $6\frac{1}{2}$ tons/in.² shortly after quenching, $8\frac{1}{2}$ tons/in.² one year later, and about $9\frac{1}{2}$ tons/in.² after two years (Table V). The properties of the aluminium-copper-cadmium alloys were slightly lower than those of the cadmium-free material. Similar effects had been noted previously, high-purity ternary alloys of aluminium-copper-indium (or tin) proving slightly softer during ageing at 30°C . than the corresponding binary aluminium-copper alloy.¹

As shown by Table VI, the production heat-treated alloys, which had been flattened, possessed higher tensile properties but underwent only slight ageing at room temperature.

(c) Artificial Ageing for Fixed Periods (Fig. 1)

Samples from the cadmium-containing alloys were solution-treated and aged for 6 hr. at temperatures between 155° and 220°C . Alloy *FZ*, with $4\frac{1}{4}\%$ copper, gave the best properties after 6 hr. at $185^\circ\text{--}190^\circ\text{C}$., whilst the alloy with 5% copper gave the highest properties after 6 hr. at $180^\circ\text{--}185^\circ\text{C}$.

TABLE IV.—Averaged Tensile-Test Results on $\text{Al-}5\%$ Cu-0.14% Cd Alloys (*GJ* and *GL*) Solution-Treated as Indicated and Aged for 6 hr. at 185°C .

Heat-Treatment		Air Furnace					Salt Bath				
Temp., $^\circ\text{C}$.	Time, min.	Alloy Ref.	Specimen Direction	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	El., %	Alloy Ref.	Specimen Direction	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	El., %
530	30	<i>GL</i>	Trans.	24.0	30.1	10
	30	<i>GL</i>	Long.	24.3	30.1	9
	30	<i>GJ</i>	Trans.	25.1	30.0	8
	30	<i>GJ</i>	Long.	24.8	30.1	$8\frac{1}{2}$	<i>GJ</i>	Long.	25.4	30.8	$8\frac{1}{2}$
	60	<i>GJ</i>	Trans.	24.6	30.3	$8\frac{1}{2}$	<i>GJ</i>	Trans.	25.3	30.4	8

GL. Production heat-treated and flattened.

GJ. Laboratory heat-treated.

TABLE V.—Averaged Transverse Tensile Properties of $Al-4\frac{1}{4}\%$ Cu (FY) and $Al-4\frac{1}{4}\%$ Cu-0.1% Cd (FZ) Alloys Solution-Treated, Cold-Water Quenched, and Aged at Room Temperature.

Ageing Time	Al-4 $\frac{1}{4}$ % Cu (FY)			Al-4 $\frac{1}{4}$ % Cu-0.1% Cd (FZ)		
	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	El., %	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	El., %
1 hr.	6.7	19.1	21	6.4	18.2	20
4 "	7.3	19.1	20 $\frac{1}{2}$	7.3	19.0	20 $\frac{1}{2}$
7 "	7.4	19.2	19	6.7	18.6	20
16 "	7.3	19.1	20	7.0	18.6	21 $\frac{1}{2}$
1 day	7.4	19.2	21	7.1	18.8	20
2 days	8.0	19.7	19 $\frac{1}{2}$	6.9	18.6	20
4 "	8.2	20.1	20	7.2	19.0	20
7 "	8.1	19.6	19	7.4	18.7	18
14 "	8.4	20.7	17	8.1	19.9	18 $\frac{1}{2}$
28 "	8.1	20.3	20	7.6	19.7	19 $\frac{1}{2}$
2 months	8.5	20.1	20	7.9	19.7	19 $\frac{1}{2}$
4 "	8.5	20.0	19 $\frac{1}{2}$	8.2	19.8	19
6 "	9.1	20.2	18 $\frac{1}{2}$	8.4	19.8	21
9 "	9.0	20.5	19 $\frac{1}{2}$	8.6	19.9	19
1 year	8.9	20.1	19 $\frac{1}{2}$	8.2	19.4	19
1 $\frac{1}{2}$ years	9.8	20.6	19	9.1	20.0	19
2 "	9.6	20.6	19	9.3	20.5	19 $\frac{1}{2}$
3 "	9.8	20.8	20	9.6	20.7	18
4 "	10.0	21.0	21	9.6	20.5	19 $\frac{1}{2}$

TABLE VI.—Averaged Tensile-Test Results on $Al-5\%$ Cu-0.14% Cd Alloy (GL) Production Solution-Treated for 30 min. at 530° C. in a Salt-Bath, Flattened, and Aged at Room Temperature.

Ageing Time	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	El., %	Erichsen Value, mm.
Nil	13.0	22.0	20 $\frac{1}{2}$...
2 months	12.6	22.9	18 $\frac{1}{2}$	8.38
3 "	12.8	23.5	20 $\frac{1}{2}$...
4 "	12.8	23.4	19	...
8 "	13.0	23.1	18	8.26
10 "	12.9	23.2	18	...
1 year	13.2	23.4	20	...
2 years	13.3	23.8	17 $\frac{1}{2}$...
2 $\frac{1}{2}$ "	13.3	23.9	18	...
3 "	13.3	24.1	20	...

Samples from the 5% copper-0.14% cadmium alloys were also aged for 24 hr. between 135° and 200° C., and, as shown in Fig. 1, the highest properties were reached after ageing at 170°-175° C. The ageing curves for the production (GL) and laboratory (GJ) heat-treated alloys were not quite identical. There was a tendency (see Fig. 1) for material GL to give higher proof-stress values than GJ when aged below 155° C., but lower values when aged between 155° and 175° C.

(d) Annealing Tests (Table VII, Fig. 2)

Samples of the aluminium-5% copper-0.14% cadmium alloys in the cold-worked (GJ) and solution-treated (GL) conditions were annealed for 30 min. at various temperatures and air-cooled. The results, summarized in Fig. 2, show that the tensile properties were unaffected by subsequent storage times be-

tween 8 weeks and 1 year. The minimum tensile properties were recorded in the case of cold-worked alloy annealed at 350° C. Higher tensile strengths were

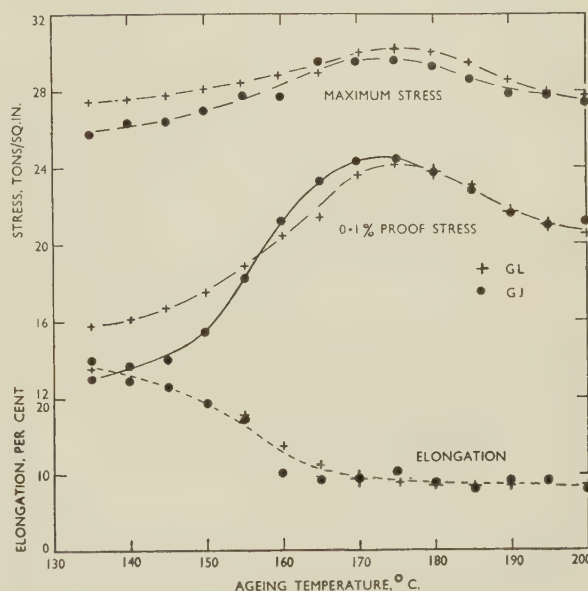


Fig. 1.—Tensile-Test Results on $Al-5\%$ Cu-0.14% Cd Alloys Solution-Treated at 530° C. and Aged for 24 Hr. at Various Temperatures. GL heat-treated in a salt bath and flattened; GJ heat-treated in air, not flattened.

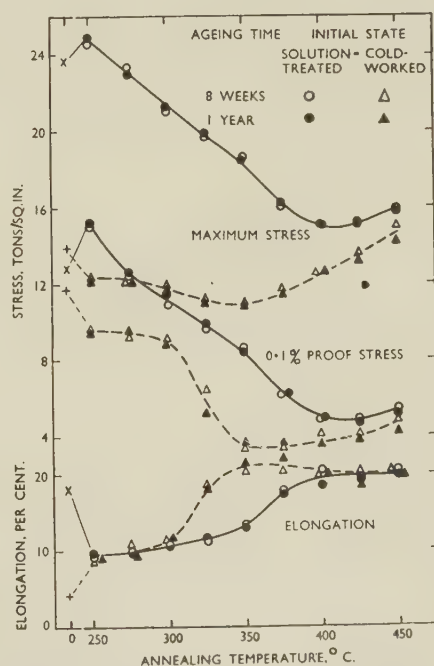


Fig. 2.—Tensile Properties of $Al-5\%$ Cu-0.14% Cd Sheet Annealed for 30 Min., Air-Cooled, and Aged at Room Temperature.

reached when the alloy was annealed from the solution-treated condition, a temperature of 400°-425° C. being needed to produce the softest condition. The two sets of curves tended to the same tensile values at

TABLE VII.—Comparison of the Effect of Air-Cooling and Furnace-Cooling on the Tensile Values of Al-5% Cu-0.14% Cd Sheet Annealed for 1 hr. and Stored for 8 Weeks at Room Temperature.

Annealing Temp., °C.	Air-Cooled				Furnace-Cooled			
	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	El., %	Erichsen Value, mm.	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	El., %	Erichsen Value, mm.
<i>Annealed from the Solution-Treated Condition (GL)</i>								
350	8.6	18.6	13½	...	8.3	17.2	16½	...
425	4.8	15.3	20½	...	4.1	12.1	22	...
<i>Annealed from the Cold-Worked Condition (GJ)</i>								
350	3.4	11.0	21	8.74	3.4	10.3	22	9.30
425	4.0	13.8	20	8.79	3.2	10.8	23½	9.02

higher annealing temperatures. As shown by Table VII, furnace-cooling gave further softening.

2. RELATION BETWEEN COLD WORK AND RESPONSE TO ARTIFICIAL AGEING

The interrelation between cold work and artificial ageing was studied on panels 8×15 in., which were solution-treated in air and quenched. These were cold worked by rolling, after which the tensile-test blanks received appropriate final ageing treatments. In reporting the results, it has frequently been found necessary to omit the multitude of experimental points from the graphs as an aid to clarity. The quoted peak values were obtained from ageing curves which are not reproduced in the present paper.

(a) Effect of Cold Work Before Artificial Ageing (Table VIII, Figs. 3 and 4)

Panels of the 4½% copper alloys (FY and FZ) were solution-treated, cold-water quenched, held for one month at room temperature, and cold rolled to 5, 10, 20, or 30% reduction. Averaged transverse tensile-

TABLE VIII.—Averaged Transverse Tensile Properties of Al-4½% Cu (FY) and Al-4½% Cu-0.1% Cd (FZ) Alloys Solution-Treated, Aged 1 Month at Room Temperature, Cold Rolled as Indicated, and Aged for 1 Year at Room Temperature.

Reduction by Cold Rolling, %	Al-4½% Cu (FY)			Al-4½% Cu-0.1% Cd (FZ)		
	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	El., %	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	El., %
Nil	8.4	20.0	19.0	8.2	19.8	18.0
5	13.8	21.4	11.4	13.8	21.3	14.4
10	16.0	21.8	9.0	16.2	22.0	9.6
20	17.9	23.1	6.3	17.6	23.0	7.8
30	18.8	24.0	5.8	18.5	24.0	6.8

test results on the cold-worked materials are given in Table VIII, from which it will be seen that the cadmium-free and cadmium-containing alloys work-hardened equally. Fig. 3 gives the ageing curves at 170° and 185° C.; similar trends were encountered at 155° and 200° C. The time to attain the peak on the ageing curves was reduced by cold working in the case of both alloys, and became substantially independent of the presence of cadmium when the cold reduction exceeded 10%. Cold work increased the maximum attainable properties given by the cadmium-free alloy. However, the alloy with cadmium exhibited the reverse effect, and the maximum properties were markedly reduced by cold working before artificial ageing.

The results are summarized in Fig. 4; in this figure the peak properties attained on ageing at the

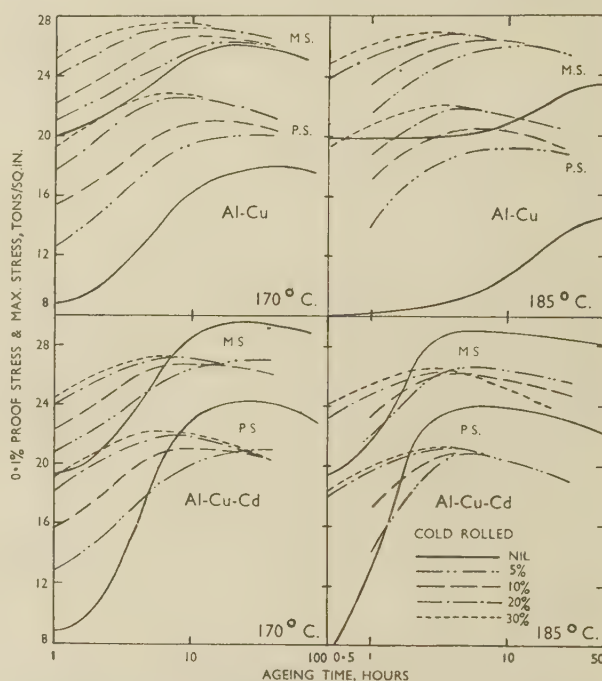


FIG. 3.—Averaged Tensile-Test Results on Al-4½% Cu (FY) and Al-4½% Cu-0.1% Cd (FZ) Alloys Solution-Treated, Cold Rolled, and Aged at 170° or 185° C.

various temperatures have been read from Fig. 3. These properties of the aluminium-copper alloy increased rapidly at first and then more slowly with increasing amounts of cold work before artificial ageing. The peak properties of the aluminium-copper-cadmium alloy passed through a minimum when it was cold rolled to 5–10% reduction. The curves in Fig. 4 would have a slightly different appearance if a constant ageing time, e.g. the time required to attain peak hardness in the absence of cold work, had been used in each case. The properties of the cadmium-free alloy would then have improved less rapidly, whilst the tensile values of the alloy with cadmium would have shown less tendency to rise after rolling more than 10%.

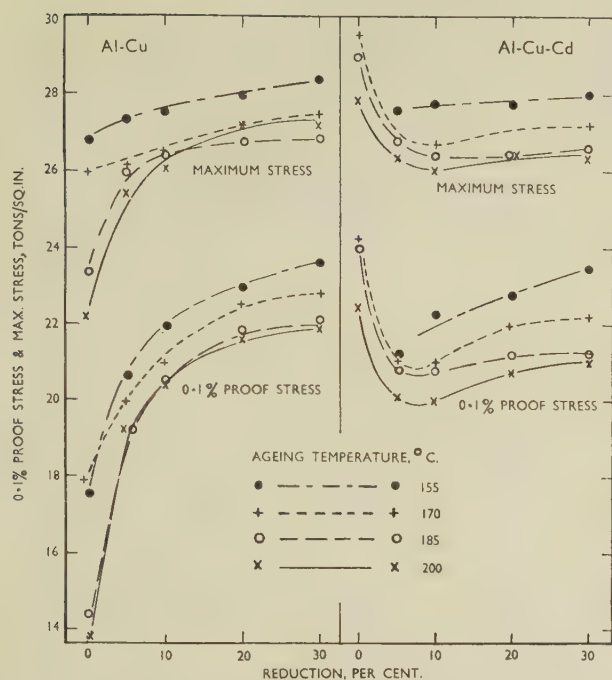


FIG. 4.—Maximum Tensile Properties of Al-41% Cu (FY) and Al-41% Cu-0.1% Cd (FZ) Alloys Attained on Ageing at Various Temperatures When Cold Rolled after Solution-Treatment.

The elongation values of the cadmium-free alloy fell with increasing amounts of cold work before ageing. A similar result occurred in the cadmium-containing alloys, but was much less marked because the

elongations were initially somewhat lower. Both alloys gave similar elongation values when cold rolled 20–30% before artificial ageing.

(b) Effect of Partial Ageing Before Cold Work
(Table IX, Figs. 5–7)

Nock⁶ has stated that the tensile properties of aluminium-copper alloys are reduced by cold working before artificial ageing, as described for aluminium-copper-cadmium alloys immediately above. He claimed that, provided that the cold work was less than 5%, the reduction in properties could be greatly minimized if the alloy had previously received a short artificial ageing treatment.

Test panels cut from the 5% copper-0.14% cadmium alloy (GJ), were therefore solution-treated in a circulating-air furnace, quenched, given various partial ageing treatments, cold rolled 6%, and finally aged. The reduction used is slightly greater than that given by Nock, but is nearer to the minimum in Fig. 4.

The results are reported in Table IX, proof-stress values greater than 23.9 tons/in.² being shown in heavy type. Pre-ageing at 155° C. had no useful effect, though ageing at 160° or 180° C. gave some improvement. The most successful pre-ageing treatment was clearly 3–6 hr. at 165° C. or 3 hr. at 170° C., combined with a final ageing treatment at 170° C.

The mechanical properties of the aluminium-copper-cadmium alloy have been shown to depend on: the pre-ageing temperature and time, the degree of cold work, and the final ageing temperature and time. In the experiments described below the pre-ageing and

TABLE IX.—Averaged Transverse Tensile-Test Results on Al-5% Cu-0.14% Cd Alloy Sheet (GJ) Solution-Treated in a Circulating-Air Furnace, Quenched in Cold Water, and Treated as Indicated.

Pre-Ageing Treatment	Aged 8 hr. at 170° C.			Aged 6 hr. at 175° C.			Aged at 180° C.		
	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	El., %	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	El., %	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	El., %
Nil	Not Cold Rolled						For 6 hr.		
Nil							26.2	31.1	8½
	Cold Rolled to 6% Reduction						22.2	28.6	8
6 hr. at 155° C.	23.9	29.7	7½	23.7	29.7	7	For 4 hr.		
3 hr. at 160° C.	23.9	29.7	8½	23.9	29.7	7½	23.8	29.6	8½
6 " " "	24.5	30.1	8	24.1	30.0	8	23.6	29.4	7½
3 hr. at 165° C.	25.0	30.2	7½	24.6	29.9	7½	24.4	30.1	7½
6 " " "	24.3	30.0	8	24.1	30.1	8	24.7	29.8	7½
1 hr. at 170° C.	23.9	29.6	8½	23.8	29.6	7½	24.1	29.9	8½
2 " " "	24.4	29.7	7	23.9	29.4	8	23.3	29.4	7
3 " " "	25.1	30.3	8	24.6	30.0	7½	24.0	29.5	7
1 hr. at 175° C.	24.2	29.7	7	24.0	29.6	7	24.7	30.0	7
2 " " "	24.3	29.6	7	23.8	29.4	7	23.9	29.4	7½
1 hr. at 180° C.	24.4	29.7	6½	24.0	29.4	7	23.7	29.3	7
2 " " "	23.2	28.6	6½	22.6	28.6	7	23.6	29.3	7½
							22.7	28.4	7

Proof-stress values greater than 23.9 tons/in.² are shown in heavy type.

final ageing treatments were both carried out at 170° C. and the remaining factors were varied.

Test panels were cut from the aluminium-5% copper-0.14% cadmium alloy sheet (*GJ*), solution-treated in a circulating-air furnace and divided into two sets. One batch was pre-aged for 3 hr. at 170° C. and both sets were given cold-rolling reductions of 5, 10, 20, or 30%. The ageing curves at 170° C. are reproduced in Fig. 5.

The material which was not pre-aged (Fig. 5 (a)) shows the same pattern of results as that in Fig. 3 for the 4.1% copper-0.1% cadmium alloy (*FZ*). Cold working decreased the time required to attain peak

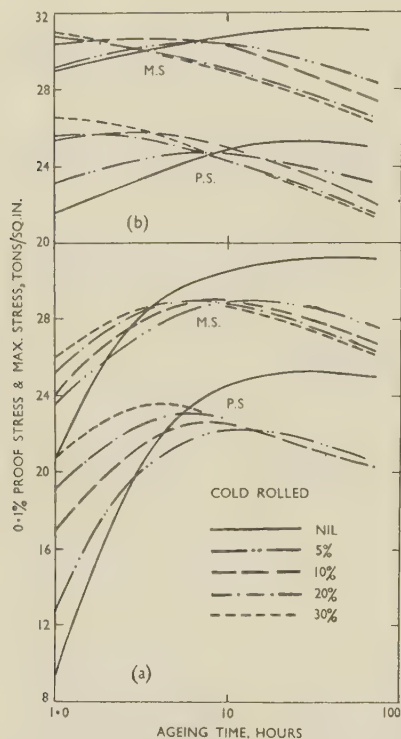


FIG. 5.—Averaged Tensile-Test Results on Al-5% Cu-0.14% Cd Alloy (*GJ*) Solution-Treated, Cold Rolled, and Aged at 170° C. (a) Not pre-aged before cold rolling. (b) Pre-aged for 3 hr. at 170° C. before cold rolling. The nil curve in (b) is the same as that in (a), but is plotted for ageing times in excess of the first 3 hr., which were counted as the incubation treatment.

properties, but also reduced both the proof- and maximum-stress values. The peak value of the proof stress after 5% cold rolling showed a minimum (Fig. 6).

A different pattern of results was met with in material given the incubation treatment before cold rolling (Fig. 5 (b)), although cold work again decreased the ageing time required to attain peak properties. The peak tensile values were slightly reduced by 5% cold work, but higher values were obtained when cold-rolling reductions were increased (see Fig. 6).

In further tests on the 5% copper-0.14% cadmium alloy (*GJ*), the pre-ageing time was varied from nil to 8 hr., the degree of cold reduction being held constant at 5%. The results, summarized in Fig. 7, show that

pre-ageing times of 2–4 hr. counteracted most of the reduction in tensile strength due to cold work. Pre-ageing times of 6 hr. and longer led to a fall in strength when the cold-worked material was further aged for

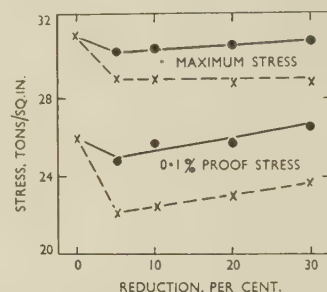


FIG. 6.—Peak Tensile Properties from Fig. 5 as a Function of the Cold Reduction.

× — × Not pre-aged before cold-rolling.
● — ● Pre-aged for 3 hr. at 170° C. before cold rolling.

2 hr. or longer. The time to attain peak properties decreased linearly from 12 hr. at 170° C. with no pre-ageing, to 2 hr. for material pre-aged for 4 hr. The best combinations of conditions to overcome the effect of 5% cold work were 2 hr. pre-ageing and 6–8 hr. final ageing or 3 hr. pre-ageing and 4–6 hr. final ageing. Both these treatments led to elongation values of about 6–8%.

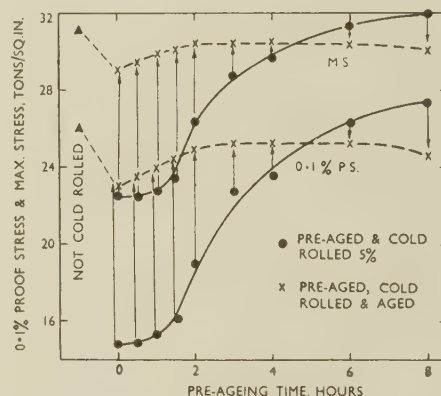


FIG. 7.—Averaged Transverse Tensile Properties of Al-5% Cu-0.14% Cd Alloy (*GJ*) Pre-Aged at 170° C., Cold Rolled 5%, and Aged at 170° C. Peak properties after ageing are given for up to 4 hr. pre-ageing; the values at 6 and 8 hr. pre-ageing are for 2 hr. at 170° C.

(c) Stress-Relief After Cold Work (Table X, Fig. 8)

The mechanism of the process by which cold work interferes with the effect of cadmium on the response of aluminium-copper alloy to age-hardening is not known. However, it was thought that a stress-relief treatment, producing recovery, might minimize the effect of cold work. The simple hypothesis predicts that stress-relief after cold work should reduce the properties of the aluminium-copper alloys and raise the properties of the aluminium-copper-cadmium alloys when finally aged.

A treatment of 2 min. in oil at 200°–220° C. reduced, by about 2 tons/in.², the proof-stress values of the aluminium-4½% copper alloy (*FY*), solution-treated and cold rolled to 5 and 10% reduction. However, 2 min. in oil at 240° C. caused less softening. The tensile properties obtained on specimens cold reduced 0, 5, or 10%, and aged to attain peak properties at 170° C., were completely independent of the stress-relief treatments of 2 min. in oil at 200°, 220°, or 240° C. (see Table X).

TABLE X.—Averaged Transverse Peak Tensile Values of Al-4½% Cu Alloy (*FY*) Stress-Relieved for 2 Min. in Oil and Aged at 170° C.

Reduction by Cold Rolling, %	0.1% Proof Stress, tons/in. ²				Maximum Stress, tons/in. ²			
	Stress-Relief				Stress-Relief			
	Nil	200° C.	220° C.	240° C.	Nil	200° C.	220° C.	240° C.
Nil	16.6	16.4	16.6	16.6	24.2	24.2	24.0	24.2
5	20.4	20.2	20.3	19.6	27.3	26.9	27.1	26.8
10	21.9	21.7	21.6	21.6	27.5	27.5	27.6	27.8

Solution-treated panels of the aluminium-5% copper-0.14% cadmium alloy (*GJ*) were cold rolled 2½, 5, 7½, or 10% and stress-relieved for 2 min. in oil at temperatures between 170° and 240° C. The fall in proof stress was about 2 tons/in.² and the gain in elongation about 5%. The peak tensile values after ageing at 170° C., given in Fig. 8, show the beneficial effect of stress-relief at 200° and 210° C. The proof stress of the material cold rolled 5% was raised by more than 2 tons/in.², and the maximum stress by more than 1 ton/in.². The stress-relief treatment proved less valuable as the amount of cold work was increased. After stress-relief and ageing the elongations measured were 6–8½%.

TABLE XI.—Stress-Corrosion Lives of Transverse Test-Pieces of Al-4½% Cu (*FY*) and Al-4½% Cu-0.1% Cd (*FZ*) Alloys Solution-Treated for 30 Min. in Air at 530° C. and Aged as Indicated.

Specimens stressed as horizontal cantilever beams and sprayed each weekday with 3% sodium chloride solution.

Al-4½% Cu (<i>FY</i>)						Al-4½% Cu-0.1% Cd (<i>FZ</i>)					
16 hr. at 165° C.		40 hr. at 165° C.		6 hr. at 185° C.		16 hr. at 165° C.		6 hr. at 185° C.		Stress, tons/in. ²	Life, days
Stress, tons/in. ²	Life, days	Stress, tons/in. ²	Life, days	Stress, tons/in. ²	Life, days	Stress, tons/in. ²	Life, days	Stress, tons/in. ²	Life, days		
18.0	4–7	18.0	21, 21	16.8	2–5, 5	25.9	195	25.9	53Y, 65Y		
17.8	4–7	16.0	13, 14	15.0	6, 12	25.7	149Y	25.0	34Y, 46Y		
17.2	4	14.0	21, 21	14.0	7, 51	24.0	162Y	24.0	27, 57		
16.8	4–7	12.0	36, 36	12.0	11, 31	23.8	213	22.0	55Y, 153		
14.0	4–7	10.0	54, 61	10.0	33, 147	22.0	195Y	20.0	60Y, 73Y		
13.6	4–7	8.0	36, 61	8.0	11, 78–83	21.9	187Y	18.0	63–68Y, 36–39Y, 78Y		
12.4	10	7.0	28, 74	17.8	220U		
10.9	4–7, 8, 10	5.0	47, 109	17.6	220U		
10.0	10, 11–14	15.0	220U, 220U	17.6	230Y		
7.0	125, 209	11.1	220U		
6.0	30–34, 212U	15.0	73Y, 94Y		
3.8	212U, 212U		

U. Test-piece unbroken.

Y. Test-piece unbroken but excessively bent.

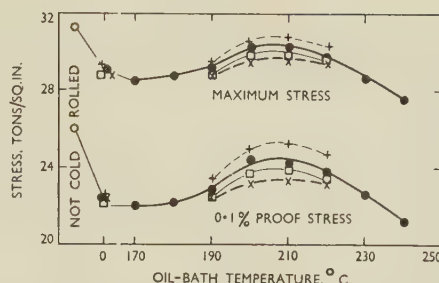


Fig. 8.—Averaged Transverse Peak Tensile Values of Al-5% Cu-0.14% Cd Alloy (*GJ*) Solution-Treated, Cold Rolled, Stress-Relieved for 2 Min. in Oil, and Aged at 170° C.

KEY.

Cold Rolled
○ Nil
+ 2½%
● 5%
Cold Rolled
□ 7½%
× 10%

3. RESISTANCE TO STRESS-CORROSION (Tables 11, 12, and 13, Figs. 9–12, Table XLVI)

Stress-corrosion tests were carried out on transverse test-pieces stressed as horizontal cantilever beams and sprayed each weekday with 3% sodium chloride solution.

Table XI gives the lives of the cadmium-free and cadmium-containing alloys with 4½% copper (*FY* and *FZ*), which had been solution-treated and aged for 16 hr. at 165° C. or 6 hr. at 185° C. The results show clearly the marked superiority of the alloy with cadmium. The cadmium-free alloy failed rapidly at stresses close to the 0.1% proof stress (see Table III, p. 338), whereas alloy *FZ* possessed a long life at stresses in excess of the proof stress. In many cases the test-pieces of this alloy were removed unbroken after 200 days, when the specimen had bent severely as a result of general corrosion. Table XI also includes results obtained on the cadmium-free alloy aged to give peak properties (40 hr.) at 165° C. The lives

at high stresses, though considerably improved, were still far below those of the cadmium-containing alloy.

The results in Table XII show that both alloys had

TABLE XII.—*Stress-Corrosion Lives of Transverse Test-Pieces of Al-4½% Cu (FY) and Al-4½% Cu-0.1% Cd (FZ) Alloys Solution-Treated for 30 Min. in Air at 530° C. and Worked and Aged as Indicated.*

Specimens stressed as horizontal cantilever beams and sprayed each weekday with 3% sodium chloride solution.

Pre-Ageing Time at 170° C., hr.	Reduction by Cold Rolling, %	Final Ageing Time at 165° C., hr.	Al-4½% Cu (FY)		Al-4½% Cu-0.1% Cd (FZ)	
			Stress, tons/in. ²	Life, days	Stress, tons/in. ²	Life, days
...	...	16	12	19, 26	22	86, 89
3	10	13, 24	12	11, 19
3	12	4, 11	14	4, 11
3	5 *	...	12	14, 14	14	14, 14
...	5	16	20	200U †	20	200U †
3	5	12	20	200U	20	200U
...	10	12	20	200U	20	200U
...	10	12	24	200U	24	200U
3	10	9	23	200U	23	200U
...	20	10	22	200U	22	200U
3	20	7	22	200U	22	200U
...	30	8	23	200U	23	200U
3	30	5	23	200U	23	200U

* Stretched, not rolled.

† All the subsequent tests were in duplicate.

U Test-piece unbroken; some of these test-pieces had yielded and bent excessively.

a low resistance when aged for 3 hr. at 170° C. The life did not exceed 14 days at stresses of 12 tons/in.² for the 4½% copper (FY) and 14 tons/in.² for the 4½% copper-0.1% cadmium (FZ) alloys, respectively. The lives were always in excess of 200 days when the materials were cold worked and finally aged to give approximately peak properties. The behaviour was then independent of the pre-ageing treatment.

TABLE XIII.—*Stress-Corrosion Lives of Transverse Test-Pieces of Al-5% Cu-0.14% Cd Alloy (GJ) Solution-Treated at 530° C., Quenched in Cold Water, and Finally Aged at 180° C.*

Specimens stressed as horizontal cantilever beams and sprayed each weekday with 3% sodium chloride solution.

Pre-Ageing Treatment	Reduction by Cold Rolling, %	Final Ageing Time at 180° C., hr.	Stress, tons/in. ²	Life, days
Nil	Nil	6	23	225U, 110, 225U, 121
"	6	6	20	225U, 182U, 182U, 225U, 182U, 182U
1 hr. at 180° C.	6	5	22	182U, 225U

U. Test-piece unbroken.

The lives recorded in Table XIII show that the 5% copper-0.14% cadmium sheet alloy (GJ), finally aged at 180° C., also possessed an excellent resistance to stress-corrosion.

The cadmium-free alloy with 4½% copper (FY),

aged for 16 hr. at 165° C. or 6 hr. at 185° C. (Table XI), exhibited severe intercrystalline corrosion (see Fig. 9, Plate XLVI). Intracrystalline corrosion occurred in the corresponding alloy with cadmium (FZ) (Fig. 10, Plate XLVI) and led to a form of layer corrosion, whilst intercrystalline corrosion was present only to a limited extent. Both the cadmium-free and cadmium-containing alloys (Table XII) gave intercrystalline corrosion when aged for 3 hr. at 170° C. On the other hand, both alloys showed predominantly intracrystalline corrosion when fully aged after cold work, either with or without the pre-ageing treatment (see Figs. 11 and 12, Plate XLVI).

Very similar microstructures were encountered in the 5% copper-0.14% cadmium alloy (GJ). Only slight intercrystalline corrosion was present in the unworked alloys aged for 6 hr. at 180° C. (Table XIII), whilst the tendency to intracrystalline corrosion was enhanced by cold work before ageing.

IV.—DISCUSSION OF RESULTS

The addition of cadmium to aluminium-copper alloys does not interfere with their excellent hot workability or affect their low capacity for ageing at room temperature. However, the introduction of cadmium causes three significant differences when the alloys are artificially aged:

(1) The tensile strength after artificial ageing is much higher than that attainable in the absence of cadmium.

(2) Although the tensile strength of aluminium-copper alloys is enhanced by cold work before artificial ageing, the aluminium-copper-cadmium alloy shows the very unusual characteristic that its tensile properties are diminished.

(3) The resistance to stress-corrosion of the artificially aged alloys is greatly enhanced by the presence of cadmium.

It is generally agreed that cold work before artificial ageing accelerates the ageing process.⁷⁻⁹ It has been reported that quite small degrees of cold work before artificial ageing significantly raise the tensile properties of Alcoa 24S alloy.¹⁰⁻¹³ Less response has been observed in 61S,¹⁴ in 75S or 14S,¹⁵ or in R.301.^{16, 17} Gunn¹⁸ gives the increase in proof stress due to 40% cold work before artificial ageing as 40, 40, 10, and 5% for 24S, D.T.D. 390, D.T.D. 546, and D.T.D. 363 alloys, respectively. The compositions of these alloys are listed in Table XIV. Hansen and Dreyer¹⁹ found augmentations in strength of aluminium-copper-magnesium alloys which had been cold worked before artificial ageing. According to Wassermann,²⁰ the hardness of an aluminium-4.13% copper alloy aged at 150° C. for less than one month was increased by 10% cold reduction. After longer ageing times, the hardness after ageing was reduced when the alloy was cold rolled but regained its former value on further ageing. The effect of cold work on the sequence of precipitates in the aluminium-4% copper

alloy has been reported by Graf and Guinier,^{21, 22} who found that, on ageing at elevated temperatures, the G.P. zones [1] and [2] were suppressed, but the formation of θ' and θ was accelerated.²³

Additions of cadmium, indium, or tin probably owe their influence on the elevated-temperature ageing of aluminium-copper alloys to some type of nucleation process¹ which favours the formation of θ' .²⁴ Cold

TABLE XIV.—Typical Alloy Compositions.

	Cu, %	Mg, %	Zn, %	Si, %	Mn, %	Cr, %
24S . . .	4.5	1.5	0.6	...
D.T.D. 390	4.3	1.0	0.75	...
61S . . .	0.25	1.0	...	0.6	...	0.25
14S . . .	4.4	0.35	...	0.8	0.75	...
R. 301 . .	4.5	0.5	...	0.9	0.8	...
D.T.D. 546	4.3	0.5	...	0.75	0.75	...
D.T.D. 363	1.5	2.0	7.0	...	0.1	0.1
75S . . .	1.6	2.5	5.7	...	0.2	0.3

work might interfere if it led to the rapid precipitation of cadmium in a form incapable of influencing the decomposition of the aluminium-copper solid solution. Alternatively, the cadmium atoms may be absorbed along dislocations,^{25, 26} and thus their normal influence on the precipitation of the copper atoms may be suppressed.* The tensile properties obtained with the cold-worked and artificially aged aluminium-copper-cadmium alloys probably represent a balance between the softening due to the effective removal of the cadmium and a hardening due to the normal nucleating effect of cold work.

The effect of pre-ageing before cold reduction is probably to produce "ternary"† nuclei, so that the precipitation process does not change back to that of the aluminium-copper alloy free from cadmium.

It may be noted that the oil-bath treatment for 2 min. at 200°–220° C. softened the solution-treated and cold-worked aluminium-copper alloys by recovery, yet had no influence on the tensile values of the material when finally aged. The effect of the stress-relief treatment on the cold-worked aluminium-copper-cadmium alloys must therefore depend on the behaviour of the cadmium atoms. A cadmium precipitate, stable up to the ageing temperature (190° C.) may be redissolved by reversion at 210° C. A more likely explanation, however, is that the cadmium is returned to effective solution by healing of the dislocations and the consequent dispersal of the cadmium atmosphere.

The enhanced general precipitation in the alloy with cadmium² reduces the possibility of a thin continuous anodic path around the grain boundaries. Consequently, the attack is predominantly intracrystalline and the fully aged sheet (e.g. 6 hr. at 180° C. or 16 hr. at 165° C.) has an excellent resistance to stress-

corrosion. Stress-corrosion may occur in material which has been only partially aged, e.g. 3 hr. at 170° C., when intercrystalline corrosion results from the difference in solution potential between the relatively undecomposed grain centres and the anodic grain-boundary regions depleted in copper by precipitation. This is in agreement with experience on other aluminium alloys, where the maximum susceptibility to intercrystalline corrosion occurs at the beginning of artificial ageing.^{27–29} The aluminium-copper alloy without cadmium showed an inferior resistance even when aged to give its peak properties (40 hr.) at 165° C. Both the cadmium-free and the cadmium-containing sheet alloys exhibited an excellent resistance when fully aged after cold work.

Previous work² has shown the superiority of cadmium over indium or tin, which have the same effect on the ageing characteristics of aluminium-copper alloys. Undissolved cadmium has less influence on the ductility at room temperature and, in small quantities, does not cause hot-shortness. Very small amounts of magnesium, which could be present

TABLE XV.—Summary of Transverse Tensile Properties of Aluminium-5% Copper-0.14% Cadmium Uncoated Sheet Alloy.

Condition	0.1% Proof Stress, tons/in. ²	Max. Stress, tons/in. ²	Elongation, %
Solution-treated	8–9	21	20
Solution-treated and aged at 170° C.	25–26	30–31	9–10
Solution-treated, cold rolled 5%	14½	28	14
Solution-treated, cold rolled 5%, aged at 170° C.	22	29	7–8
Solution-treated, aged for 3 hr. at 170° C.	20	28	12
Solution-treated, aged for 3 hr. at 170° C., rolled 5%	22	29	6–8
Solution-treated, aged for 3 hr. at 170° C., rolled 5%, aged at 170° C.	25	30	6–8
Solution-treated, cold rolled 5%, stress-relieved for 2 min. at 200°–210° C.	11	21	17½
Solution-treated, cold rolled 5%, stress-relieved for 2 min. at 200°–210° C., aged at 170° C.	24	30	6–8

incidentally, do not affect the alloys of aluminium and copper with cadmium, but they restrain the normal influence of tin or indium, so that lower tensile properties are found after artificial ageing. Very small quantities of magnesium change the ageing characteristics of aluminium-copper-indium and aluminium-copper-tin alloys towards those of aluminium-copper alloys. It is therefore probable that the presence of magnesium would alter adversely the stress-corrosion

* 0.1 wt.-% of cadmium gives approximately 1.5×10^{19} cadmium atoms/cm.³ of alloy. The dislocation density of annealed and cold-worked materials may be taken as 10^{16} and 10^{20} A./cm.³, respectively. The length of the dislocations

in a cold-worked material is therefore sufficient to absorb an appreciable fraction of the cadmium atoms.

† No specific mechanism is implied by this term.

resistance of aluminium-copper-indium and aluminium-copper-tin alloys. The ageing of aluminium-copper-cadmium alloys is not affected by small quantities of magnesium so that their resistance to stress-corrosion would also be unimpaired.

The tensile properties of the aluminium-5% copper-0.14% cadmium alloy are summarized in Table XV. The reduction in strength due to cold work may be minimized either by pre-ageing or stress-relief. The freedom from natural ageing means that the quenched sheet can be stored indefinitely with no deterioration

in the forming characteristics. It also renders the alloy suitable for flash-annealing followed by rapid cooling.⁴

ACKNOWLEDGEMENTS

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REFERENCES

1. H. K. Hardy, *J. Inst. Metals*, 1951-52, **80**, 483.
2. H. K. Hardy, *ibid.*, 1950-51, **78**, 169.
3. H. K. Hardy, *ibid.*, 1950-51, **78**, 657.
4. E. A. G. Liddiard and H. K. Hardy, *Rep. Congr. Sci. Internat. Aluminium (Paris)*, 1954, (in the press).
5. E. Scheuer, *J. Inst. Metals*, 1949, **76**, 103.
6. J. A. Nock, Jr., U.S. Patent No. **2,083,576**, 1937.
7. R. W. Lindsay and J. T. Norton, *Trans. Amer. Inst. Min. Met. Eng.*, 1939, **133**, 111.
8. M. L. V. Gayler, *J. Inst. Metals*, 1946, **72**, 543.
9. B. L. Averbach, *Cold Working of Metals (Amer. Soc. Metals)*, 1949, 262.
10. K. R. Jackman, *Aviation*, 1943, **42**, (8), 154; (9), 168; (10), 156.
11. B. Mitchell, *J. Aeronaut. Sci.*, 1943, **10**, (3), 86.
12. P. P. Mozley, *ibid.*, 1943, **10**, (6), 180.
13. M. E. Tatman and R. A. Miller, *Iron Age*, 1944, **153**, (4), 50.
14. J. J. Warga, *Trans. Amer. Soc. Metals*, 1947, **39**, 680.
15. E. H. Dix, Jr., *ibid.*, 1945, **35**, 130.
16. T. L. Fritzlen and L. F. Mondolfo, *Metals and Alloys*, 1944, **20**, 926.
17. T. L. Fritzlen and L. F. Mondolfo, *Metal Progress*, 1945, **47**, 1129.
18. K. Gunn, *J. Roy. Aeronaut. Soc.*, 1950, **54**, 400.
19. M. Hansen and K. L. Dreyer, *Aluminium*, 1940, **22**, 134.
20. G. Wassermann, *Z. Metallkunde*, 1950, **41**, 50.
21. R. Graf and A. Guinier, *Compt. rend.*, 1954, **238**, (7), 819.
22. R. Graf and A. Guinier, *ibid.*, 1954, **238**, (22), 2175.
23. J. Silcock, T. J. Heal, and H. K. Hardy, *J. Inst. Metals*, 1953-54, **82**, 239.
24. I. J. Polmear and H. K. Hardy, *ibid.*, 1952-53, **81**, 427.
25. A. H. Cottrell, "Progress in Metal Physics", Vol. 1, p. 77. Edited by B. Chalmers. 1949: London (Butterworths Scientific Publications).
26. A. H. Cottrell, "Progress in Metal Physics", Vol. 4, p. 205. Edited by B. Chalmers. 1953: London (Pergamon Press, Ltd.).
27. K. L. Meissner, *J. Inst. Metals*, 1931, **45**, 187.
28. W. D. Robertson, *Trans. Amer. Inst. Min. Met. Eng.*, 1946, **166**, 216.
29. H. L. Logan, H. Hessing, and H. E. Francis, *J. Research Nat. Bur. Stand.*, 1947, **38**, 465.

A HOT IMPACT TENSILE TEST AND ITS RELATION TO HOT-WORKING PROPERTIES *

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(Communication from The British Non-Ferrous Metals Research Association)

SYNOPSIS

A simple attachment to a standard Izod impact machine permits tensile test-pieces to be broken at strain rates of about 250 sec.⁻¹. By mounting a furnace close to the machine, the tests can be carried out at a high temperature by rapidly transferring the specimen from the furnace to the anvil of the machine.

The behaviour of a variety of copper-base materials in the test has been compared with their known working behaviour. A comparison has also been made between the ductility shown by a bronze in the test and its liability to edge cracking in hot rolling at various temperatures.

I.—INTRODUCTION

A NEED frequently arises for a simple, rapid laboratory test which can be used to assess the hot workability of materials. This need is particularly felt when it is desired to explore the effects of a wide range of variables, as, e.g., in studies of the effects of impurities in relation to heat-treatment and working temperature. Such a test can hardly be expected to cover all the relevant properties, since in general it will not simulate the repeated alternate deformation and recovery which are often involved in hot working. A suitable test, however, should certainly give a measure of the ductility of the material under appropriate conditions in a single deformation, and this may well be the most important single property measurable.

None of the tests already available for this purpose is entirely satisfactory. To carry out the normal type of tensile test is usually a slow procedure at high temperatures, since each specimen must be separately preheated on the testing machine and the temperature stabilized during the test. Moreover, the rate of straining is much less than in most hot-working operations, and this difference may render the results misleading. Use has often been made of forging tests, in which a cylindrical test-sample is reduced by pressing between plates, or by a hammer blow, to a fraction of the original height. Such tests can be highly informative, but results may be affected by conditions of test which are difficult to specify and, moreover, the results cannot easily be expressed quantitatively. Notched-bar Charpy-type impact tests have also been used, but these have serious disadvantages. The presence of the notch makes the

test very sensitive to slight embrittlement of a ductile material, and moreover, in the range of ductility which is critical in hot working, the sensitivity to small changes is low because uniformly low impact values are obtained. A further disadvantage of this type of test is that it provides no direct quantitative measure of ductility, and hence it is impossible to compare materials of different stiffness or even to compare samples of the same material tested at different temperatures. High-speed torsion tests appear to have some advantages,¹ although there are complications, one of which is that there is in general no single direction of maximum stress relative to the texture of the material.

The impact tensile test described here was adopted in order to avoid these various difficulties, and five years' experience of its use in these laboratories has shown it to be convenient and useful. The experiments now described were carried out in order to establish clearly the relations between results obtained and hot-working properties of the materials tested. A number of copper-base alloys of well-known working behaviour were tested, including brasses, bronzes, and coppers with various amounts of bismuth. Further experiments were carried out on a bronze to establish the relationship between the ductility shown in the test and the liability to edge cracking in the hot rolling of strip; Bourne (in unpublished work carried out at the British Iron and Steel Research Association Laboratories) has shown that, for cold rolling, a simple relationship exists between the reduction for edge cracking (for a round edge) and the reduction in area in an ordinary (cold) tensile test, and it was felt that an analogous relationship might be found in the present case.

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results of Voce and Hallows' notched-bar tests on the same materials. Study of this figure reveals that the impact tensile test is likely to be the more suitable for examination of rather brittle material, as a given quantity of bismuth does not produce such a large relative fall in the measured values as it does in the

less than 10 min. The tin bronzes had previously been given a homogenizing treatment of 4 hr. at 625° C.

TABLE II.—Analyses of Commercial Copper Alloys Tested.

	Cu, %	Bi, %	Pb, %
Brasses	62.1	0.0001	<0.001
	63.3	0.0002	<0.001
	65.3	0.0002	<0.001
	80.1	0.0001	<0.001
Aluminium Bronzes	93.4	0.0002	<0.001
	90.4	0.0004	<0.001
Tin Bronzes :			
	Nom. 5% Sn, 0.1% P	...	0.0010
	" 8% Sn, 0.1% P	tr. <0.0001	0.0022

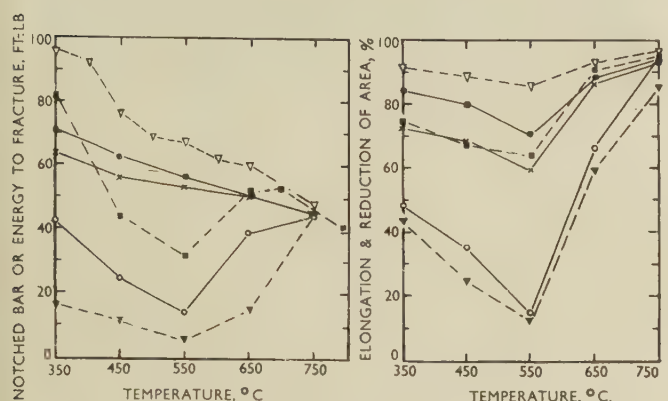


FIG. 3.—Impact Tensile and Notched-Bar Tests on Bismuth-Containing Coppers.

other test. The test has the obvious advantage that it gives two direct measures (elongation and reduction in area at fracture) of the capacity of a material for hot deformation, whereas the notched-bar value is a function of both the amount of deformation before fracture and the force required to effect the deformation.

The reduction-of-area values in the above tests on rectangular specimens were difficult to measure because of the concave-sided fractures, and accordingly subsequent specimens were normally made with cylindrical gauge-lengths.

IV.—TESTS ON COMMERCIAL CAST COPPER-BASE ALLOYS

Chill-cast brasses, bronzes, and aluminium bronzes, of which the hot-working characteristics are well known, were tested at temperatures from room temperature to 850° or 900° C. Analyses for copper and for the principal embrittling impurities, lead and bismuth, are given in Table II. Test results are plotted in Figs. 4–6. Up to 350° C., the results are of single tests; at 450° C. and above, they are the mean results of two.

The cast billets were about 4½ in. in dia., and the specimens were taken transversely from the region of equiaxial macrostructure, except for the alloy with the highest zinc content, in which columnar grains extended to the centre. The specimens from this alloy were taken so that the gauge-length lay across the columnar grains. Before testing, the specimens were preheated for ½ hr., reaching test temperature in

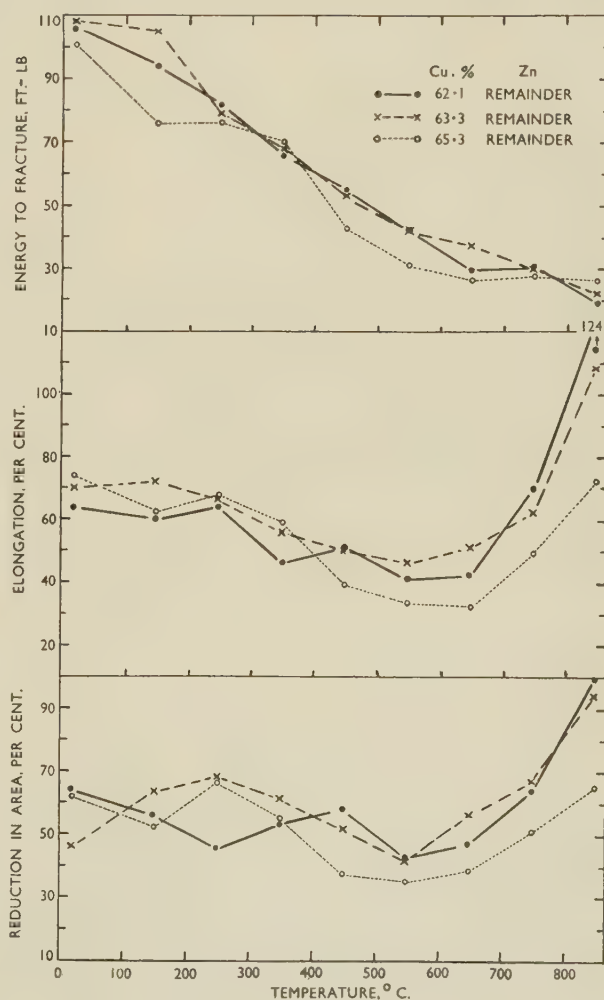


FIG. 4.—Impact Tensile Tests on Some Cast Brasses.

Spectrographic analyses of the alloys revealed no other impurities likely to affect their working behaviour.

Because these were cast materials, there was inevitably some scatter in the properties, which is

reflected in the irregularity of the lines in Figs. 4-6, but the general effects of temperature and composition are clearly shown. Fig. 4 illustrates the effect of variation in the amount of β phase present at hot-working temperatures. In each of the three brasses the ductility falls slowly with temperature up to 500°-600° C. and then rises steeply as the proportion of β increases, reaching a very high value for the

sumably owing to the breakdown of the β phase into α and the brittle γ_2 . At higher temperatures this alloy, like the high-zinc brasses, exhibits the expected large progressive increase in ductility as the proportion of β rises.

Thus, in the alloys specially suitable for hot working, the test reflects the marked increase in ductility as the alloys pass into the hot-working range. The tin bronzes (Fig. 6), on the other hand, are found in the test to incur a large loss of ductility at hot-working

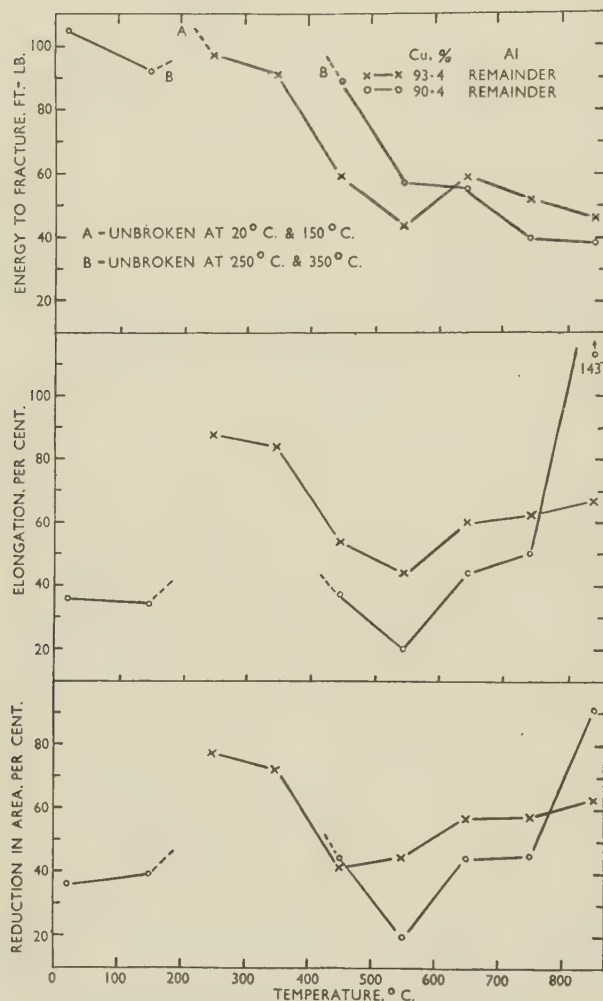


FIG. 5.—Impact Tensile Tests on Cast Aluminium Bronzes.

62 : 38 alloy at 850° C. The 80 : 20 α -phase brass, on the other hand (Fig. 6), has a sustained, moderately high ductility throughout the temperature range.

The aluminium bronzes behave much as expected. The ductility of the α -phase alloys is high at the lowest temperatures (the specimens being unbroken at room temperature and 150° C.) and falls somewhat as the temperature is raised, with a pronounced minimum at about 500° C. Other, unpublished, work shows that this minimum is attributable to the presence of bismuth; even smaller quantities than the 0.0002% here present have a measurable effect in this alloy. The 9½% aluminium alloy undergoes a marked fall in ductility just below the eutectoid temperature, pre-

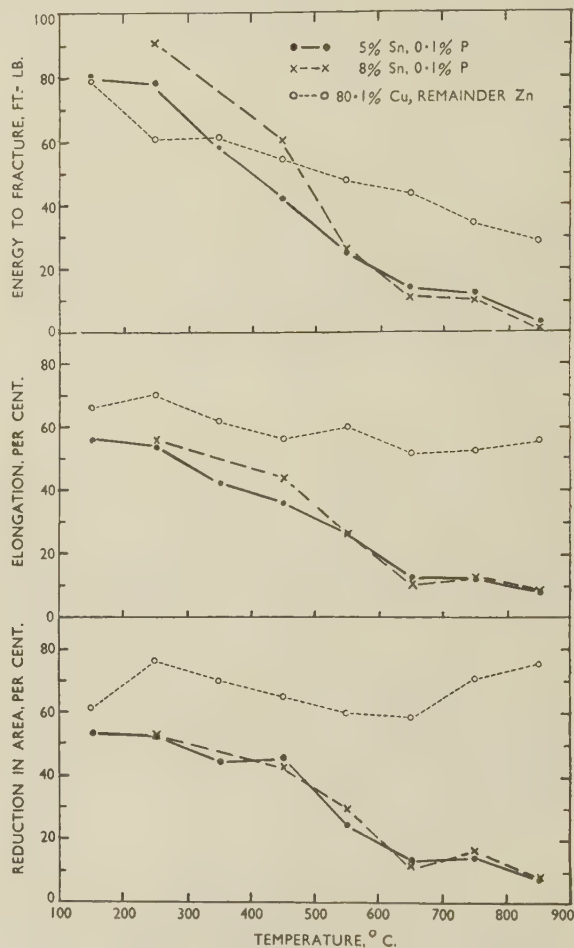


FIG. 6.—Impact Tensile Tests on Cast Tin Bronzes and 80 : 20 Brass.

temperatures, consistent with their very poor hot-working behaviour.³

In this test, the energy to fracture divided by the elongation gives an indication of the average force required to produce the extension. For instance, from the results in Fig. 4, it appears that at high temperatures this force requirement decreases with increasing zinc content in the (α + β) brasses and is less for them than for the α -brass (Fig. 6). This average force, however, is only a very approximate measure of the stiffness in working operations because of the variable amount of work-hardening arising from different extensions in the test.

V.—QUANTITATIVE CORRELATION WITH EDGE CRACKING IN HOT-ROLLING EXPERIMENTS ON AN 8% TIN BRONZE

In conjunction with an investigation of the properties of tin bronzes, experiments have been made to establish the relation between the ductility, as determined in the hot impact tensile test, and the edge cracking which is liable to occur in the hot rolling of strip. In rolling strip or sheet, edge cracking may not in itself be of great importance, provided that it does not spread unduly across the strip. Nevertheless, it is a typical example of the cracking at unsupported places and high temperatures to which these materials are especially prone, and which cannot be tolerated in the rolling of rod and sections.

Hessenberg⁴ has referred to experiments with several metals on the edge cracking of strip during cold rolling. As is usual, edge cracking is attributed to the development of high longitudinal tensile stresses at the edge, which are more severe for a round edge than a square one, since the former is less well supported by the rolls. Bourne, in unpublished experiments of the British Iron and Steel Research Association on the same materials, has found a simple relationship between the reduction causing cracking in cold rolling, for an edge of semi-circular section, and the reduction in area at fracture in a tensile test. This is: (reduction for cracking in rolling) = $1.4 \times$ (reduction in area in tensile test).

The present experiments were designed to show whether a similar relationship exists for hot rolling and the impact tensile test. Observations were restricted to a single pass through the rolls, since behaviour in continued rolling is complicated by recovery or recrystallization between passes. The experiments covered the temperature range 600°–850° C., giving a range of behaviour.

1. MATERIALS

The bronze specimens tested contained approximately 8% tin and 0.1% phosphorus, and were obtained from bars chill-cast from cathode copper and "Chempur" tin.

By analysis the several samples used were found to contain: 7.7–8.2% Sn (by difference), 0.08–0.13% P, <0.0005–0.0017% Pb, <0.0001–0.00015% Bi, <0.0007% As, and 0.0009–0.0035% Sb. The castings contained small amounts of interdendritic microporosity, and the densities of slices from near the tops of the cast bars were 8.85–8.90 g./c.c.

The castings were cropped and cut up as shown in Fig. 7. The wrought material was prepared from machined pieces approximately $1\frac{3}{4}$ in. square (Fig. 7). These were partially homogenized by heating at 625° C. for 1 hr., cold rolled to 1-in.-thick strip, annealed, pickled, and cold rolled further to a thickness of 0.55 in. The strips were then straightened and further homogenized at 625° C. for 11 hr. in nitrogen.

The test-pieces of the cast material were homogenized at 625° C. for 12 hr., in nitrogen.

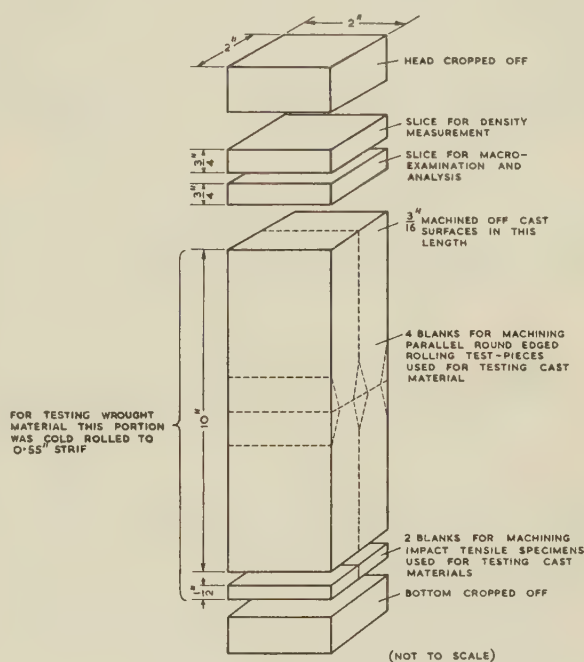


FIG. 7.—Sectioning of Castings.

The average grain diameters of the cast and wrought materials, before testing, were 0.5–0.7 and 0.04–0.07 mm. respectively.

2. IMPACT TENSILE TESTS

Duplicate specimens were tested, at 50° C. intervals. All were held at the testing temperature for $\frac{1}{2}$ hr.

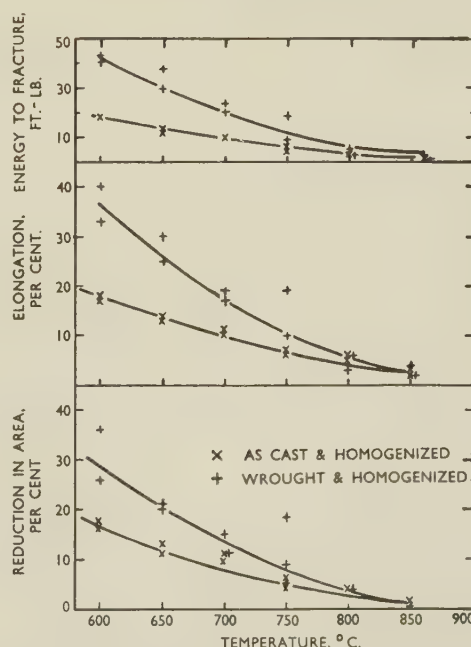


FIG. 8.—Impact Tensile Tests on Wrought and Cast 8% Tin–0.08% Phosphorus Bronze.

before testing. The results are plotted in Fig. 8 (coincident results are given as a single point). It appeared that incipient melting had occurred at 850° C.

3. ROLLING EXPERIMENTS

Rolling was carried out on a two-high mill with 12-in.-dia. rolls turning at 23 r.p.m. The surfaces of

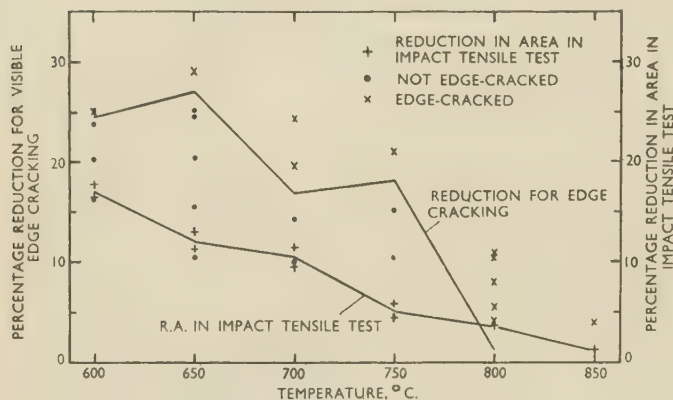


Fig. 9.—Reductions for Edge Cracking in Rolling Round-Edged Test-Pieces at Various Temperatures Compared with Reductions in Area in Impact Tensile Tests on Cast Material.

the rolls were lubricated with mineral oil and preheated to about 60°–80° C. The entry table of the mill was covered with a thin sheet of asbestos board which carried a single asbestos guide to assist in putting

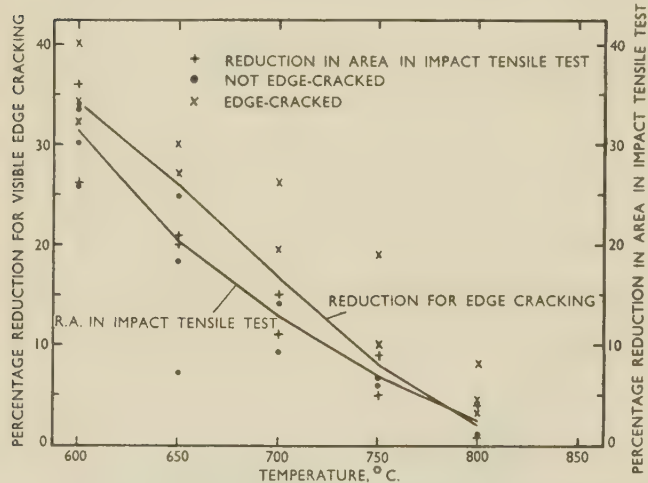


Fig. 10.—Reductions for Edge Cracking in Rolling Round-Edged Test-Pieces at Various Temperatures Compared with Reductions in Area in Impact Tensile Tests on Wrought Material.

in the bar straight. An electric muffle furnace for preheating was placed close to the entry table, and the time taken to withdraw a bar from the furnace, place it against the guide, and insert it into the rolls, was less than 2 sec.

Two sizes of test-piece were used, both having parallel faces except for a short tapered nose to facilitate entry into the rolls. Details were as follows :

(1) Cast and homogenized : 1.625 in. wide, 0.75 in. thick, tapered 10° at one end to 0.4 in., 5 in. long, with edges having 0.375 in. radius.

(2) Wrought and homogenized : 1.625 in. wide, 0.5 in. thick, tapered 10° at one end to 0.35 in., 5 in. long with edges having 0.25 in. radius.

A number of specimens were each given a single pass through the rolls, with successively reduced roll-gap settings, and the reductions which did or did not produce visible edge cracking were noted. Generally, when cracking occurred the extent was fairly uniform along the length. Where only one or two small cracks at the extreme back end of the test-piece were observed they were disregarded. At 850° C. very small reductions (less than 2%) resulted in extensive cracking throughout the test-piece, with evidence of incipient melting.

The results are presented graphically in Figs. 9 and 10, which also include the values obtained for reductions of area in impact tensile tests at similar temperatures.

4. RELATION BETWEEN RESULTS OF IMPACT TENSILE TESTS AND ROLLING EXPERIMENTS

In Fig. 11 the reductions for edge cracking in rolling these round-edged specimens (from Figs. 9 and 10) are

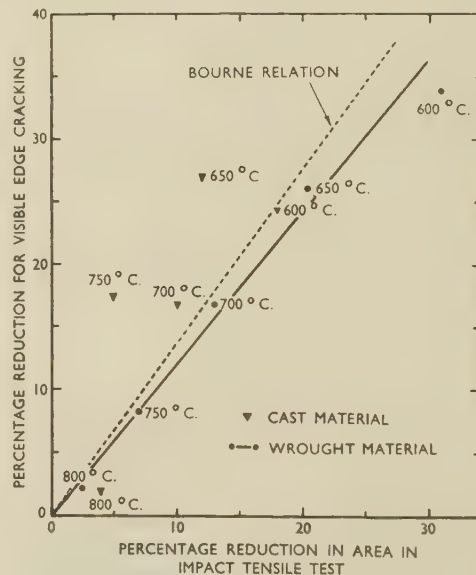


Fig. 11.—Relation between Rolling Reductions Causing Edge-Cracking (Round-Edged Test-Pieces) and Reduction in Area in Impact Tensile Tests.

plotted against the mean reductions in area obtained in impact tensile tests at the same temperature. For the wrought material, the results between 650° and 800° C. are in good agreement with the relation proposed by Bourne. At 600° C. there is considerable deviation from the relation, but, in view of the nature of the tests, this may be due to scatter, and, taking this into account, the results on the whole are quite well represented by a constant of 1.2, in place of the

1.4 of Bourne's relation. For the cast material, owing to the large scatter of the results, it is not possible to draw firm conclusions.

VI.—DISCUSSION AND CONCLUSIONS

From the experiments reported it appears that the hot impact tensile test does yield results which are closely related to the behaviour of metals in hot-working operations. In one case a quantitative relationship has been demonstrated, and, although under other conditions this will not be valid, there seems little doubt that the ductility in simple tension is a good guide to behaviour in working.

The rate of elongation in the test, with the standard Izod machine which is available, is initially approximately 260 sec.^{-1} , falling as energy is absorbed by the specimen. Rates approaching this occur in hot stamping and similar operations. In hot rolling the rate is not usually as high; probably $5\text{--}10 \text{ sec.}^{-1}$ would be typical. In an ordinary tensile test the rate is of the order of $1 \times 10^{-3} \text{ sec.}^{-1}$ or nearly 10^4 times

slower again. Thus the impact tensile test is a better approximation to practical conditions. It might be preferable to use a somewhat slower rate of deformation than the test at present provides, if a suitable machine were available; the same type of arrangement and procedure could still be used. However, it seems better to utilize standard equipment, especially as working speeds are constantly being increased.

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REFERENCES

1. D. E. R. Hughes, *J. Iron Steel Inst.*, 1952, **170**, 214.
2. E. Voce and A. P. C. Hallows, *J. Inst. Metals*, 1947, **73**, 323.
3. D. W. D. Showell, *ibid.*, 1949-50, **76**, 527.
4. W. C. F. Hesselberg, *ibid.*, 1948-49, **75**, 1173 (discussion).

1603 LATTICE SPACINGS OF THE ALUMINIUM-RICH SOLID SOLUTION CONTAINING MAGNESIUM AND SILICON*

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SYNOPSIS

Measurements of the lattice spacing of alloys in the aluminium-rich ternary solid solution containing magnesium and silicon are reported. A negative deviation from simple additivity is encountered, the magnitude of which increases with increasing alloy content of the solid solution. The results are interpreted as indicating a degree of attractive interaction between the dissimilar solute atoms in the ternary solid solution.

I.—EXPERIMENTAL METHODS

LATTICE-SPACING relationships in the aluminium-rich solid solutions of the aluminium-magnesium and aluminium-magnesium-copper systems have already been published.¹ The present paper reports an extension of the investigation to the aluminium-rich solid solution of the aluminium-magnesium-silicon system. The materials used in the present investigation were the super-purity aluminium and spectrographically pure magnesium previously described,¹ together with a sample of aluminium-silicon master alloy made up from an aluminium base of 99.998% purity and containing 11.8% silicon and 0.046% iron by analysis. The experimental methods have been described in detail elsewhere,¹⁻⁴ and hence it is necessary only to indicate that the ingot was annealed at 536° C. for 7 days and the filings were annealed at 536° C. for 1 hr. Micrographic examination of the homogenized ingots was undertaken to confirm the absence of a second phase. The specimen temperature was maintained constant to within 0.5° C. during an exposure. All lattice-spacing values were corrected to a temperature of 25° C., using a value of 23.1×10^{-6} as the coefficient of expansion of the dilute solid-solution alloys.¹ No correction was made for refraction.

Copper radiation was used and the wave-length of $\text{CuK}\alpha_1$ was taken as 1.537395 and that of $\text{CuK}\alpha_2$ as 1.541232, the final results being given in kX units.

II.—EXPERIMENTAL RESULTS

Table I shows the analysed compositions of all the X-ray powder specimens, and it will be seen that they are all within a reasonable distance from one or other of the four lines of constant alloy content for 0.72, 1.08, 1.26, and 1.42% of alloying element, respectively. Table I also shows the corrections in composition required to bring the analysed points exactly on to

one of these four lines. It will be noted that alloy compositions on the magnesium-rich side of the quasi-binary Al-Mg₂Si line were corrected for mag-

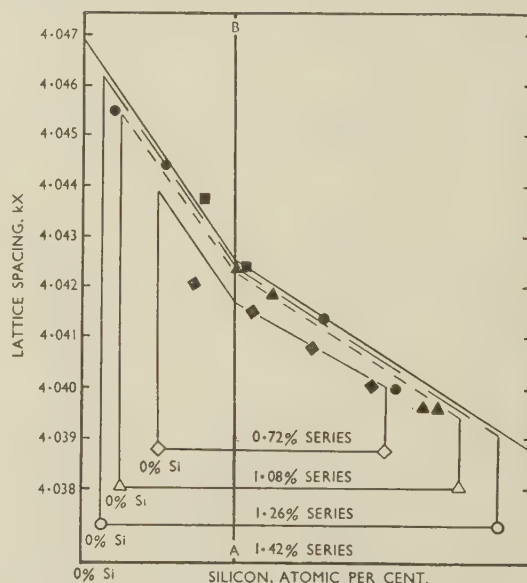


Fig. 1.—Variation of Lattice Spacing with Composition. The corrected values of the lattice spacings of all the alloys investigated in the ternary solid solution are shown to the same lattice-spacing scale. The alloys are grouped into four series containing 0.72 (◆), 1.08 (▲), 1.26 (●), and 1.42% (■) of alloying element, respectively, and the composition base-line for each series is so arranged that it intersects the quasi-binary Al-Mg₂Si line along AB. A uniform composition scale is used and the lengths of the composition base-lines, as denoted by the open symbols, are proportional to the alloy-contents of the particular series. The left-hand end of each base-line corresponds to 0% silicon in the particular series.

nesium only, whereas those on the silicon-rich side were corrected for silicon value only. These corrections are shown as ΔM and ΔS in Table I. The corrections of lattice spacings which would correspond to ΔM and ΔS in the binary systems^{2, 1} are shown as.

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ΔaM and ΔaS in Table I, and, in correcting lattice spacings for composition, it is assumed that the silicon correction is independent of the total quantity of magnesium present and vice versa. From the discussion which follows it will be obvious that this is not accurately true, and it is significant that the points in Fig. 1 which show most deviation from the proposed lattice-spacing relationship in the ternary solid solution are those for which the correction ΔaM is particularly large.

used for the binary limits are, for the magnesium edge :

0.72% Mg	4.0439(5) kX
1.08% Mg	4.0455(0) kX
1.26% Mg	4.0462(8) kX
1.42% Mg	4.0469(7) kX

and for the silicon edge :

0.72% Si	4.0400(3) kX
1.08% Si	4.0394(0) kX
1.26% Si	4.0390(7) kX
1.42% Si	4.0387(7) kX

TABLE I.—*The Correction of Observed Lattice Spacings to the Values Used in Fig. 1.*

Magnesium of "Specpure" quality. Data corrected to 25° C.

Alloy Series	Analysis		Correct to :		Correction		Lattice-Spacing Corrections		Observed Lattice Spacing, kX	Corrected Lattice Spacing, kX
	Mg, at.-%	Si, at.-%	Mg, at.-%	Si, at.-%	ΔM	ΔS	ΔaM	ΔaS		
0.72	0.72	...	0.72	4.0439(5)
	...	0.72	...	0.72	4.0400(3)
	0.565	0.11	0.61	0.11	+0.045	...	+0.000165	...	4.0418(6)	4.0420(2)
	0.43	0.30	0.42	0.30	-0.01	...	-0.000036	...	4.0415(3)	4.0415(0)
	0.23	0.51	0.23	0.49	...	-0.02	...	+0.000036	4.0407(2)	4.0407(5)
	0.04	0.72	0.04	0.68	...	-0.04	...	+0.000072	4.0398(5)	4.0399(2)
1.08	1.08	...	1.08	4.0455(0)
	...	1.08	...	1.08	4.0394(0)
	0.74	0.365	0.715	0.365	-0.025	...	-0.00009	...	4.0425(0)	4.0424(1)
	0.60	0.48	0.60	0.48	4.0418(6)	4.0418(6)
	0.12	1.00	0.12	0.96	...	-0.04	...	+0.000072	4.0394(2)	4.0394(9)
	0.03	1.03	0.03	1.05	...	+0.02	...	-0.000036	4.0394(2)	4.0393(8)
1.26	1.26	...	1.26	4.0462(8)
	...	1.26	...	1.26	4.0390(7)
	1.26	0.05	1.21	0.05	-0.05	...	-0.00018	...	4.0456(2)	4.0454(4)
	1.10	0.20	1.06	0.20	-0.04	...	-0.00014	...	4.0446(0)	4.0444(6)
	0.555	0.73	0.555	0.705	...	-0.025	...	+0.000045	4.0413(7)	4.0414(1)
	0.33	0.87	0.33	0.93	...	+0.06	...	-0.000108	4.0400(3)	4.0399(2)
1.42	1.42	...	1.42	4.0469(7)
	...	1.42	...	1.42	4.0387(7)
	1.05	0.385	1.035	0.385	-0.015	...	-0.000054	...	4.0438(1)	4.0437(6)
	0.90	0.54	0.90	0.52	...	-0.02	...	+0.000036	4.0423(7)	4.0424(0)

The corrected values of lattice spacings are shown in Fig. 1, where the variation of lattice spacing for the four lines of constant alloy content has been plotted in such a way that the lattice-spacing scale is common to all the results, whilst four separate composition base-lines are used. The composition base-line which ends in open diamonds corresponds to the alloys on the 0.72%-alloy-content line of an equilateral ternary composition plane; the composition base-line ending in open circles in Fig. 1 corresponds to alloys on the 1.26%-alloy-content line of the same equilateral ternary composition plane, and so on. It will be noted that the composition base-lines of Fig. 1 have been so arranged that the line *AB* represents the intersection of the quasi-binary line Al-Mg₂Si of the equilateral ternary composition plane with the various base-lines in this figure. The lattice spacings at the binary limits of the four composition base-lines are taken from the "Specpure" magnesium curve of Poole and Axon¹ and from the linear relationship found for the aluminium-silicon solid solution by Axon and Hume-Rothery,² which was confirmed in the course of the present work. The actual values

III.—DISCUSSION

The total extent of solid solubility in this ternary system is so small, and the variation of lattice spacing with composition so rapid, that the normal uncertainties in the chemical analysis of the two solute metals combine to result in a rather large total uncertainty. Moreover, in considering any one of the four composition series, it is obvious that no single series contains sufficient alloys to provide an unambiguous lattice-spacing relationship within the series. On the other hand, the compositions for the four series taken together provide a reasonable coverage within the ternary solid solution. Thus, without placing too much weight on the absolute value of particular measurements and considering the results for all four series taken together, it appears that the lattice-spacing relationship within the ternary solid solution may be represented by two plane surfaces which meet along the Al-Mg₂Si quasi-binary line and extend outwards to the magnesium and silicon binary walls, respectively. Such a pair of planes represents an unambiguous negative deviation of lattice spacing

from the linear relationship which might be expected from the purely additive effects of the two solute elements considered separately. Moreover, this negative deviation reaches a maximum value along the quasi-binary line *AB* of Fig. 1, and suggests an attractive interaction between the dissolved magnesium and the dissolved silicon. A similar minimum has been reported in the electrical resistivity of the ternary solid-solution alloys and has been interpreted as indicating a deviation from random distribution in the solid solution in a manner akin to chemical molecule formation.⁵ In this context one must not attempt to ascribe too detailed a geometrical pattern to the "molecule"; certainly there is no suggestion that the "molecule" exists with the Mg_2Si crystal structure, since the " Mg_2Si structure" presupposes the presence of many atoms of magnesium and of silicon packed regularly together in the correct proportions.

In Fig. 1, the magnitude of the negative deviation (i.e. the difference between the lattice spacing which would result from a linear variation of lattice spacing between the binary end members of a series and the experimental values for that series) may be obtained with fair confidence for the 1.42% and the 1.08% series, in which there are experimental points near to, or on, the quasi-binary line. Additional values may be obtained for the other two series if the validity of the bi-linear relationship which meets at the quasi-binary is assumed. The four values of the negative deviation so obtained indicate that the deviation increases in a linear manner as the Mg_2Si content is increased along the quasi-binary line. If this effect is extrapolated to 100% of alloying element, i.e. to the composition Mg_2Si , a value of 0.13 kX is obtained for the negative deviation.

It has already been pointed out¹ that the closest distance of approach of atoms in a crystal of Mg_2Si is

2.75 kX, whereas the mean interatomic distance calculated for the additive effect of magnesium and silicon atoms in the ratio 2:1 is 2.9 kX; the negative deviation in this case being 0.15 kX. This may be taken as a general confirmation that the negative deviation found in the aluminium-rich solid solution is associated with some form of clustering between magnesium and silicon atoms in solution such that, along the quasi-binary line, the effect of magnesium and silicon on the lattice spacing of the solid solution lies between the effect expected from the atoms acting independently and that expected of Mg_2Si "molecules" in solution.

A further point of interest is to determine the value of the particular magnesium:silicon ratio in the ternary solid solution which produces no variation from the lattice spacing of aluminium. If the bi-planar representation of the ternary lattice spacings is assumed, it is found that this value is approximately 4 Mg to 5 Si atoms.

ACKNOWLEDGEMENTS

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REFERENCES

1. D. M. Poole and H. J. Axon, *J. Inst. Metals*, 1951-52, **80**, 599.
2. H. J. Axon and W. Hume-Rothery, *Proc. Roy. Soc.*, 1948, [A], **193**, 1.
3. R. B. Hill and H. J. Axon, *Research*, 1953, **6**, (4), 23s.
4. H. J. Axon, A. Hellawell, D. M. Poole, and W. Hume-Rothery, *Brit. J. Appl. Physics*, 1953, **4**, 188.
5. T. A. Badaeva, *Doklady Akad. Nauk. S.S.S.R.*, 1949, **64**, 533.

SOME OBSERVATIONS ON ISOTHERMAL TRANSFORMATIONS OF EUTECTOID ALUMINIUM BRONZES BELOW THEIR M_s TEMPERATURES *

1604

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SYNOPSIS

Microstructural changes occurring during transformations of three aluminium bronzes below their M_s temperatures are described. It is suggested that isothermal formation of martensite occurs and that both martensite and the phase from which it forms may transform to eutectoid. Small additions of nickel to the binary alloys depress the M_s temperatures and increase the rates of transformation.

I.—INTRODUCTION

SMITH and Lindlief ¹ and Mack ² have described transformations of eutectoid copper-aluminium alloys below the M_s temperature, and their observations are similar to those made on the binary alloy used in the present work, which was carried out as part of an investigation into isothermal transformations of aluminium bronzes and of the effect of small amounts of nickel on them.

II.—EXPERIMENTAL

1. ALLOYS AND METHODS

The preparation of the alloys, with compositions as shown in Table I, and the method of effecting isothermal transformation, have been described previously.^{3,4} The transformations were followed by microscopic examination, the etching reagents employed being 1% aqueous chromic acid solution, used electrolytically,⁵ and ammonia and hydrogen peroxide.¹

TABLE I.—Compositions and M_s Temperatures of Alloys.

Alloy No.	M_s Temp., °C.	Cu, %	Al, %	Ni, %	Fe, %	Si, %
2	400–378	87.76	12.20	0.00	0.04	Trace
4	400–373	86.68	12.45	0.87	Trace	0.00
6	473–350	84.85	12.07	3.08	„	0.00

* By difference.

2. RESULTS

The M_s temperatures for β_1 lie in the temperature ranges shown in Table I. Microstructural changes occurring in “ β ” ‡ were studied, using the chromic

acid reagent, which does not reveal the structure of β' formed on quenching.

(a) Transformation of Alloy 2 at 378° C.

After 30 sec. the “ β ” had a faint acicular appearance and fine precipitate was present in some grain boundaries. The structure after about 1 hr. (Fig. 1, Plate XLVII) showed fine needles which seemed to be crystallographically related to the acicular structure. The acicular appearance became clearer, and the fine needles increased in number, as time elapsed.

Nodules of eutectoid were present after 5 hr., and the amount of eutectoid increased with time, but transformation was incomplete after 2 weeks. Eutectoid (Fig. 2, Plate XLVII) grew most quickly in areas which contained fine needles; it was partly spheroidized.

In specimens transformed for at least 2 days, a phase similar to the matrix phase of the duplex constituent in specimens transformed at 350° C. occurred adjacent to some grain boundaries in regions which had transformed to eutectoid.

(b) Transformation of Alloy 2 at 350° C.

A fine grain-boundary precipitate appeared within 30 sec., and the “ β ” had a faint acicular appearance. Within about a week, the acicular appearance became clearer, and fine needles were present in some parts; in specimens transformed for much longer periods, however, the “ β ” appeared almost structureless.

A duplex precipitate (Fig. 3, Plate XLVII) was present at some grain boundaries after 5 days, the quantity of it increasing very slowly with time; after 5 weeks about 15% was present. The precipitate (Figs. 3 and 4, Plate XLVII) consisted of ragged bluish-coloured particles in a twinned pink matrix, which absorbed grain-boundary α and grew erratically, often enclosing pools of “ β ”. The pink phase could

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‡ “ β ” is used to denote the mixture of β_1 and β' formed during and after quenching in the isothermal bath.

not be distinguished from " β " when etched with the chromic acid solution. Tempering at 500° C. caused the bluish particles in the duplex precipitate to become more numerous and larger, and the " β " to decompose into $\alpha + \gamma_2$. These observations suggest that the duplex precipitate may consist of particles of γ_2 in a matrix of α supersaturated with aluminium.

(c) *Transformations of Alloy 4 at 373° C. and 350° C.*

The transformations of Alloy 4 were similar to each other, that occurring at 350° C. being much the slower.

Grain-boundary α precipitate was present after 1 min., and in a few minutes " β " showed a coarse acicular structure having fine needles within certain parts of it (Fig. 5, Plate XLVIII). Alternate bands of the acicular structure were yellow and pink, and the interfaces between them were slightly curved. Fine needles crossed only pink bands and crossed neither yellow bands nor each other. For several days the needles increased in number, especially in regions where there were few yellow bands; but after 3 weeks at 350° C., the " β " appeared almost structureless.

Nodules of eutectoid were present after 1½ hr., and a day, at 373° and 350° C., respectively, and " β " gradually transformed to eutectoid (Fig. 6, Plate XLVIII). Transformation occurred most quickly in pink bands of " β ", and the eutectoid was spheroidal. Transformation at 373° C. was almost complete after 2 weeks, but at 350° C. it was still incomplete after 5 weeks.

(d) *Transformation of Alloy 6 at 350° C.*

Fine grain-boundary precipitate was present within 30 sec. The structure after 5 min. (Figs. 7 and 8, Plate XLVIII) showed many very thin, long, dark-etching needles intermixed with a coarser acicular structure. The dark-etching needles increased in number very rapidly with time (Figs. 9 and 10, Plate XLIX) and gave the microstructure a somewhat confused appearance. Eventually, the coarser acicular structure (Fig. 11, Plate XLIX) became clearer, but some fine needles still remained. Spheroidal eutectoid (Fig. 12, Plate XLIX) was detected after 6 hr., and the transformation was complete within 5–12 days.

III.—DISCUSSION OF RESULTS

When an alloy is cooled below its M_s temperature, the amount of β' formed depends on the degree of

undercooling, the remainder of the material remaining as β_1 . With lapse of time at temperature, fine needles appear in the microstructure and increase in number over a period of about a week; they can, however, no longer be seen in samples held for two or more weeks. These changes may represent the isothermal formation of β' , and " β " will appear structureless when this transformation is complete.

Eutectoid appears after an induction period, growing most quickly in the phase of " β " in which fine needles form, and eventually the alloy changes completely to eutectoid. Close to the M_s temperature, eutectoid forms from both β_1 and β' , and β_1 transforms to eutectoid as it does above the M_s temperature. Formation of eutectoid from β' may occur either directly, as in Alloys 4 and 6, or in two stages, as in Alloy 2. These two stages may represent the formation of α supersaturated with aluminium, followed by precipitation of γ_2 from α . The transformations in Alloys 4 and 6 may also occur in two stages, the second taking place more quickly than the first, so that no supersaturated solid solution is observed in the microstructure. It is probable that the phase in which the eutectoid grows most quickly is β_1 , since growth occurs most rapidly in parts of the acicular structure in which fine needles form; moreover, the driving force for the transformation $\beta_1 \rightarrow \alpha + \gamma_2$ is greater than that for $\beta' \rightarrow \alpha + \gamma_2$.

Small amounts of nickel added to binary alloys depress the M_s temperatures and increase the rates of transformation below the M_s temperatures.

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REFERENCES

1. C. S. Smith and W. E. Lindlief, *Trans. Amer. Inst. Min. Met. Eng.*, 1933, **104**, 69.
2. D. J. Mack, *ibid.*, 1948, **175**, 240.
3. R. Haynes, *J. Inst. Metals*, 1953–54, **82**, (10), 493.
4. R. Haynes, *ibid.*, 1954–55, **83**, (3), 105.
5. W. C. Coons and D. J. Blickwede, *Trans. Amer. Soc. Metals*, 1945, **35**, 284.

THE METALLOGRAPHIC DETECTION OF DEFORMATION IN COPPER AND ALPHA-BRASSES*

1605

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SYNOPSIS

A systematic survey has been made of the effectiveness of a wide range of etching techniques in detecting evidence of deformation in a tough-pitch copper and a series of α -brasses. The nature of the metallographic indications has also been investigated, principally by a taper-sectioning technique. It has been found that four distinct types of indication can be developed, the two most important types being referred to as slip-line and slip-band indications, respectively. Slip-line indications are developed by a limited number of etching techniques only, but may be found at very low strains ($<0.1\%$ deformation in 70 : 30 brass). They are shown to be associated with (optically) single slip lines. Slip-band indications are developed easily in α -brasses by all etching methods, and are the classical strain markings. They are thought to be associated with the formation of coarse lamellar slip bands.

The information obtained has enabled some conclusions to be drawn as to the fundamental slip processes of α -brasses, both at the surface and in the interior of the material.

I.—INTRODUCTION

ALTHOUGH it has been well known since the earliest days of metallography that indications of deformation can frequently be developed by suitable etching techniques, it is only in recent years that the phenomenon has been systematically investigated. Even so, attention has been confined mainly to copper alloys, in which the indications can be easily developed by standard etching reagents.

The classical indications detected in copper alloys, which have been variously termed "strain markings", "etch markings", "etch bands", or "deformation lines", have been shown to be associated with a definite crystallographic plane in each grain (the 111 plane),¹⁻³ and it has been assumed that they are associated with the slip process. Most investigations have been carried out on high-zinc α -brasses of the 70 : 30 type, but many different etching techniques have been used, and the sensitivity reported for the development of indications has varied over wide limits. Brick¹ and Brick and Williamson² detected indications in 70 : 30 brass at 20% deformation, Cook and Richards⁴ at 10% deformation, McLean⁵ at least at 2% deformation, Burke and Barrett³ at 1% deformation, and Hibbard *et al.*⁶ at 5% deformation. Jacquet^{7,8} developed a special electrolytic-etching technique for 70 : 30 brass, and it was thought that indications could be developed at the first detectable stages of slip. The etching methods used by these investigators are tabulated in the Appendix (p. 367).

A limited amount of work has also been carried out on pure copper. Cook and Richards^{9,10} failed to detect any evidence of deformation other than elongation of the grains at low deformations, although etching indications associated with deformation bands were

detected at deformations above 40–50%. Jacquet,¹¹ however, has described an electrolytic-etching technique which was stated to develop prominent "striations" at 5% deformation and even faint indications at 1.5%. Hibbard *et al.*⁶ also detected indications at about 9% deformation.

In view of these conflicting results, it was decided to carry out a systematic investigation in which copper and a series of α -brasses were deformed by progressively increasing amounts and then examined metallographically after etching in a wide range of reagents. The work was extended to obtain some further information as to the nature of the metallographic indications.

II.—EXPERIMENTAL METHODS

1. PREPARATION OF SPECIMENS

The materials investigated were a tough-pitch high-conductivity copper and a series of commercial copper-zinc alloys of the chemical compositions listed in Table I. With the exception of the 97 : 3 brass, which was in plate form, the material was in the form of rod approximately 1 cm. in dia. The rods were cut into cylinders approximately 1 cm. in length, the ends of which were turned flat and parallel; the plate was cut into approximately 1-cm. cubes. The copper cylinders were annealed at 550°C. for 30 min., and all the brasses at 650°C. for 30 min.; the final grain-size of the annealed material is shown in Table I.

It will be noted that the grain-size of the 90 : 10 brass was considerably coarser than that of the remaining alloys; it is unlikely, however, that this will affect the type of deformation indication developed, a conclusion supported by the results of Hibbard *et al.*⁶ The buttons were finally compressed by light cold

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hammering to the required amount, using reductions of 2.5%, 5%, 10%, 15%, 20%, and thereafter in 10% steps. It might well be expected that the method of deformation could influence the stage at which the

TABLE I.—*Chemical Composition and Grain-Size of Alloys.*

Alloy	Content, wt.-%				Mean Grain Dia., mm.
	Copper	Oxygen	Arsenic	Zinc *	
Copper	0.017	0.04
97 : 3 Brass . .	96.8	3.2	0.07
90 : 10 Brass . .	89.1	...	0.05	10.8	0.40
85 : 15 Brass . .	84.8	15.2	0.07
80 : 20 Brass . .	80.6	19.4	0.09
70 : 30 Brass . .	70.3	...	0.05	29.6	0.06

* By difference. Spectrographic traces only of other elements.

various deformation indications were developed, and a preliminary investigation has indicated that this is, in fact, so. The present results therefore apply quantitatively only to this particular method of deformation.

A specimen of 70 : 30 brass was also produced containing a gradation of very small deformations. A length of rod was machined to a rectangular cross-section with a slight longitudinal taper, annealed at 650° C. for 30 min., and given a light pass in a small rolling mill such that deformations increasing uniformly from 0 to 2.0% compression were developed along a known length of the specimen.

2. METALLOGRAPHIC TECHNIQUE

The compressed cylinders were sectioned diametrically in a plane parallel to the compression direction and hot-mounted under pressure in Bakelite by the normal metallographic method. The sections were first prepared by mechanical polishing to the (0-1) μ -grade diamond abrasive pad, using the technique previously described by the author.¹² They were finish-polished in a Jacquet¹¹ orthophosphoric acid, electrolytic-polishing bath. Brief details of the etching techniques used are set out in the Appendix (p. 367).

A preliminary examination indicated that the most satisfactory method of comparing different etching techniques was to determine microscopically the proportion of grains in which indications were developed after a certain amount of deformation, as recommended by Hibbard *et al.*⁶ The grain counts were carried out on the central portion only of the specimens, and a total count of 300-400 grains was made in each case; repeat counts indicated the results to be reproducible to approximately $\pm 2\%$. They were usually made under slightly oblique illumination, which is considerably more sensitive than vertical illumination for detecting the fainter indications, and doubtful grains were examined with the illumination decentred successively in two perpendicular directions. Perry-

man and Lack¹³ have reported that phase-contrast illumination is particularly suitable for detecting these indications. Although this was confirmed to some extent, no features additional to those described here were detected under phase-contrast illumination, and the results of grain counts were unchanged. The microscopic examination was generally carried out at a standard magnification of $\times 500$, and all the accompanying micrographs are at that magnification. The micrographs are arranged with the compression direction parallel to their longer side.

III.—RESULTS OF METALLOGRAPHIC EXAMINATION

At an early stage, it was noted that metallographic indications of deformation took a variety of forms and, as the work proceeded, it became apparent that these indications could be classified into four distinct groups having general characteristics as follows:

Type I.—Systems of parallel grooves or lines of etch pits, oriented according to the crystallographic planes of the particular grains in which they occurred. Developed at low deformations.

Type II.—Relatively wide bands oriented similarly to those of Type I, and apparently a development of them. Developed after low to medium deformations.

Type III.—Two sets of parallel lines, the orientations of which were related to the direction of compression and not to those of the grains. Developed after medium to heavy deformations.

Type IV.—Two sets of parallel undulations, the orientations of which were related to the direction of compression, but at different angles to those of the Type III indications. Developed only after heavy deformations.

As will be seen from the descriptions which follow, the precise form of the indications varied according to the material and the etching reagent employed. Type II indications were not observed in unalloyed copper, and Type III indications were observed only in copper and the low-zinc brasses.

1. COPPER

(a) Type I Indications

The electrolytic thiosulphate etch (both high- and low-sensitivity conditions gave the same results) was the only etching technique examined which produced indications in copper at low deformations. These indications, which are referred to as Type I indications, appeared to be systems of parallel lines of etch pits and usually extended completely across the individual grains (Fig. 5, Plate L). Only 4% of the grains contained indications at 2.5% compression, but the indications became both more numerous and more marked at higher deformations, and eventually appeared as definite lines (Fig. 6, Plate L). Indications were present in 45-50% of the grains at 20% compression (Fig. 1).

(b) Type III Indications

At deformations of the order of 20–30% compression, an additional indication of somewhat different appearance could be distinguished after an electrolytic thiosulphate etch. The new indications, which will be termed Type III, were very marked and, when well developed, were always present as two systems of

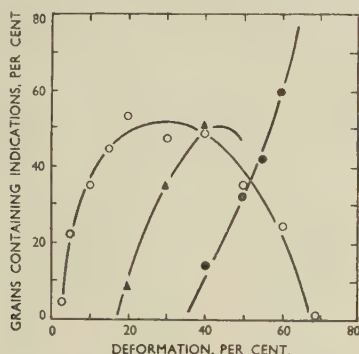


Fig. 1.—Grain Counts of Indications Developed in Tough-Pitch Copper.

KEY.

- Electrolytic thiosulphate etch (Types I and III).
- ▲ Potassium dichromate etch (Type III).
- Ammonium hydroxide-hydrogen peroxide etch (Type IV).

constant orientation. Each system was inclined at 70°–75° to the compression direction (Fig. 7, Plate L). They could be reasonably clearly distinguished from Type I, even when both were present together.

The Type III indications appeared to develop only in those grains which would have contained Type I indications. They reached their maximum development at about 40% compression (Fig. 7, Plate L), when they had completely replaced the Type I. The indications thereafter decreased rapidly in both intensity and degree of development (Fig. 8, Plate L), and entirely disappeared by 70% compression. The complete grain count of the indications developed by the electrolytic thiosulphate etch is shown in Fig. 1; the maximum in the curve at 20–40% compression is associated with the appearance and disappearance of the Type III indications.

Although none of the remaining etching techniques investigated was successful in developing Type I indications, all readily developed the Type III. A typical micrograph obtained with the potassium dichromate etch is shown in Fig. 9 (Plate L), and the results of grain counts after this etch are shown in Fig. 1. A comparison of these results with those reported by Hibbard *et al.*⁶ suggests that the indications detected by these workers in pure copper were those referred to here as Type III. The results obtained at deformations in the range 50–60% compression with relief etches, such as the potassium dichromate reagent, were somewhat confused, possibly because of interference by the Type IV indications discussed below. The Type III indications could not then be clearly distinguished, and the relevant curve in Fig. 1 has therefore been discontinued at 40% compression.

The short-circuit etch recommended by Jacquet¹¹ for pure copper failed to develop either of the above indications if the conditions were such as to cause redeposition of copper on the surface. Fresh phosphoric acid solutions developed marked etch facets in the low-deformation specimens, which might be interpreted as evidence of deformation, but such an interpretation in the specimens examined here is considered very doubtful. In any event, the etch was not comparable with the electrolytic thiosulphate etch for developing evidence of small amounts of deformation. At higher deformations, the etch developed the Type III indications reasonably clearly.

(c) Type IV Indications

Heavy attack by several of the relief etches, such as the potassium dichromate and ammonium hydroxide-hydrogen peroxide reagents, developed a further type of indication in high-deformation specimens. The indications were faint surface undulations uniformly orientated throughout the specimen at 55°–60° to the compression direction (Fig. 10, Plate L). These indications appeared to be of the type reported by Cook and Richards.^{9, 10} Counts of the indications, which are subsequently referred to as Type IV indications, are also shown in Fig. 1.

The development of these indications coincides with the disappearance of the Type III. The Types III and IV indications could not be developed clearly together, and so no relationship could be established between the two. Apparently they are distinct metallographic types; the Type III are much more easily developed than the Type IV indications and show a different angular relationship.

2. 70 : 30 BRASS

(a) Type I Indications

The electrolytic thiosulphate etch was again successful in developing indications at low deformations in the 70 : 30 brass. The indications were generally similar to those found in copper, and will again be termed Type I indications. The high-sensitivity etch developed extensive indications in all the grains at 2.5% compression (see Fig. 14, Plate LI), and even in all the grains of annealed specimens which had been deformed only during the process of hot mounting in Bakelite. Since the deformation of the specimens during mounting is very slight, it is apparent that the elevated temperature at which any deformation occurs is the important factor in the development of the Type I indications. The first development of the indications was therefore more conveniently investigated in the taper-rolled specimen referred to in Section II, 1; the specimen was sectioned longitudinally and mounted by casting in a cold-setting polyester resin.

The first indications developed in this specimen by the high-sensitivity electrolytic thiosulphate etch consisted of short dark lines which were confined largely to areas adjacent to the twin and grain

boundaries. These lines were also associated with a differential colouring effect which extended considerably further into the body of the grains (Fig. 12, Plate L). The coloured bands were noted by Jacquet,⁸ who thought them a separate type of indication. However, they were usually associated with the dark bounding lines, and an etch of slightly lower sensitivity (0.25% solution at 1 amp./dm.²) did not develop the coloured bands but only lines of etch pits at the positions of the previous dark lines (Fig. 13, Plate LI).^{*} The coloured bands appear to be an effect associated with normal Type I indications, and no distinction has been made between the two in this paper.

Indications were detected after etching under each of the above conditions at the point marked as zero compression in the taper-rolled specimen. It is difficult, however, to be certain of the exact position of this point, so that the first evidence of deformation under these conditions is reported as <0.1% compression. The deformations at which indications were first developed to the same extent as that shown in Fig. 13 (Plate LI) by various other combinations of the electrolytic thiosulphate etch are set out in Table II.

TABLE II.—Approximate Minimum Deformation for the Detection of Deformation Indications in 70 : 30 Brass.

Type of Etch	Compression, %
Electrolytic thiosulphate etch :	
0.25% soln.; 3.5 amp./dm. ² *	<0.1
0.25% soln.; 1.0 amp./dm. ² .	<0.1
0.5% soln.; 3.5 amp./dm. ² .	0.1–0.15
0.5% soln.; 1.0 amp./dm. ² † .	0.15–0.2
1.0% soln.; 3.5 amp./dm. ² .	0.15–0.2
1.0% soln.; 1.0 amp./dm. ² .	0.4–0.45
Ammonium hydroxide–hydrogen peroxide reagent	<0.1
Cupric ammonium chloride reagent .	0.45–0.5
Electrolytic polishing cell etch .	0.7–0.8

* Standard high-sensitivity etch.

† Standard low-sensitivity etch.

Although the standard high- and low-sensitivity etches both developed indications at approximately the same deformation, there was an important difference in the etch produced under the two conditions. The high-sensitivity etch gave little or no grain-colour contrast and developed indications in all grains at even the lowest deformations. The sensitivity of the etch was so high that it was only by very careful handling and preparation that annealed material could be obtained completely free from indications (Fig. 11, Plate L†). The other combinations listed gave increasing grain-colour contrast and gave indications only in the lighter-etching grains (cf. Fig. 12, Plate L, and Fig. 13, Plate LI); the indications developed in individual grains were also less numerous.

* Since this work was completed, Jacquet³⁹ has described exactly similar etch-pitting effects.

Only three of the remaining etching techniques investigated were capable of developing Type I indications reliably under normal etching conditions, namely: the ammonium hydroxide–hydrogen peroxide reagent (Fig. 18, Plate LI), the cupric ammonium chloride reagent and the electrolytic polishing cell etch (Fig. 19, Plate LI). All these methods developed the indications as grooves which were most clearly seen under oblique illumination. The sensitivity of the ammonium hydroxide–hydrogen peroxide reagent was indistinguishable in the present tests from that of the high-sensitivity electrolytic thiosulphate etch, but the other two methods were of slightly lower sensitivity (Fig. 2, and Table II).

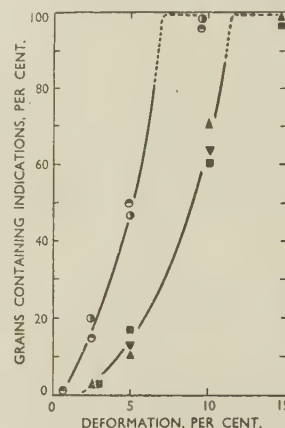


Fig. 2.—Grain Counts of Indications Developed in 70 : 30 Brass.

KEY.

- Electrolytic cell etch (Types I and II).
- Cupric ammonium chloride etch (Types I and II).
- ▲ Potassium dichromate etch (Type II).
- Ferric chloride etch (Type II).
- ▼ Phosphoric acid etch (Type II).

Again, the indications developed first at areas adjacent to the grain and twin boundaries (Fig. 19, Plate LI). Occasionally, some faint traces of indications were also developed by the ferric chloride reagent, but these effects did not seem to be reproducible.

(b) Type II Indications

It was apparent that, at 5–10% compression, all the etching methods which develop the Type I indications were also developing a second distinct type of indication. The new indications, which will be termed Type II, were discrete bands which first developed along the Type I at the grain and twin boundaries and then gradually extended into the grains (Figs. 16 and 18, Plate LI). The Type II indications developed rapidly both in number and extent at higher deformations at the expense of the Type I and gradually replaced the latter type (Fig. 17, Plate LI).

Type II indications were easily revealed by all the etching techniques investigated, but their appearance depended to some extent upon the severity of etching. The indications developed by light etching could be

† This specimen was prepared entirely by the mechanical polishing method described elsewhere.¹²

resolved into a series of fine parallel lines showing translations at the intersections of two systems, as previously described by Burke and Barrett.³ Indications developed by heavier etching with colouring reagents appeared as discrete unresolvable coloured bands (Fig. 21, Plate LII); heavier attack with relief etches, such as the ammonium hydroxide-hydrogen peroxide and potassium dichromate reagents, developed the indications as marked grooves (Fig. 18, Plate LI).

The results obtained with the potassium dichromate reagent were identical with those illustrated by Hibbard *et al.*,⁶ and it is clear that the indications investigated by these authors are those referred to here as Type II. The phosphoric acid reagent also develops Type II indications only (Fig. 22, Plate LII), and a comparison of micrographs confirms that the "striations" developed by McLean⁵ in the tapered tensile specimen were also solely of this type.*

The results of grain counts after etching with reagents of this group, which indicate the sensitivity with which Type II indications are developed alone, are shown in Fig. 2; all etches gave essentially the same counts. So far as the development in individual grains is concerned, the indications were very extensive and numerous at 20% compression (Fig. 21, Plate LII), but decreased fairly rapidly in both number and extent as the deformation decreased. They were virtually confined to areas immediately adjacent to the grain boundaries at 5% compression (Fig. 22, Plate LII), and the only evidence of the indications at 2.5% compression was a few short lines at the grain boundary. No definite Type II indications were found in the taper-rolled specimen at the maximum deformation of approximately 2% compression.

All the above characteristics suggest that the Type II indications are closely related to, and a development of, the Type I. This conclusion was further supported by the observations in a coarse-grained specimen of groups of Type I indications in the vicinity of the grain boundaries (Fig. 15, Plate LI). These groups appear to form a transition stage between the two types.

(c) Type IV Indications

Constant-orientation indications similar to those found in copper were first detected at deformations of about 50% compression. The microstructure at these intermediate deformations was very confused, and it was not possible to distinguish with certainty between the Types II and IV indications until about 70–80% compression had been effected (Fig. 20, Plate LI). These indications also were readily etched by all methods.

3. LOWER-ZINC BRASSES

The characteristics of lower-zinc brasses were generally similar to those of the 70 : 30 brass, but the

sensitivity of all etching treatments in developing indications decreased with decreasing zinc content. The change in sensitivity of representative etches, as assessed by the deformation required to develop indications in 20% of the grains, is indicated in Fig. 4. The approximate minimum deformation at which indications were developed in each alloy is shown in Table III; these values were mostly determined by extrapolating the grain-count curves.

TABLE III.—Approximate Minimum Deformation for the Detection of Deformation Indications in α -Brasses.

Zinc, % (Nominal)	Compression, %		
	Type I *	Type II	Type III
0	1.5	...	17
3	3.0	50	25
10	2.5	9	...
15	1.0	7	...
20	0.5	4.5	...
30	<0.1	2	...

* Electrolytic thiosulphate etch.

The low-grain-contrast etch with which the high sensitivity was associated in the 70 : 30 brasses could not be obtained in these alloys with any of the combinations of the electrolytic thiosulphate etch. Further, the indications were progressively less clearly developed and appeared as grooves rather than sharp lines. In the case of the ammonium hydroxide-hydrogen peroxide etch, the Type I indications were also considerably less clearly developed at lower zinc contents; they were only just detectable in the 85 : 15 brass and were not seen at all in the 90 : 10 brass. The sensitivity of the etch in this range was similar to that shown in Fig. 4 for the electrolytic thiosulphate etch. The electrolytic polishing cell and cupric ammonium chloride etches failed to reveal evidence of Type I indications in any of the lower-zinc alloys.

The sensitivity of development of Type II indications also decreased with decreasing zinc content, but these indications were still clearly developed in all alloys by all etching methods. The sensitivity curve for the Type II indications shown in Fig. 4 was actually determined with the ferric chloride reagent, but is generally representative. This curve is in good agreement with that reported by Hibbard *et al.*⁶ at intermediate zinc contents, but the minimum in the curve at 20% zinc reported by these workers has not been confirmed.

A notable characteristic of the Type II indications was that they increased appreciably in width as the zinc content decreased, the maximum width being attained at about 10% zinc (cf. Figs. 21, 23, 24, and 26, Plate LII). The increase in width was not associated with grain-size, since coarsening the 70 : 30 brass to a mean grain diameter of 0.4 mm. did

* In McLean's investigation, the hammered cylindrical specimens were etched in a cupric ammonium chloride reagent and Type I indications were developed. The tapered

tensile test-piece specimens were etched in a phosphoric acid reagent.¹⁴

not alter the width of the indications. The colour contrast of the broad indications in the low-zinc brasses was sometimes reversed, i.e. they appeared as light bands in dark-etching grains (Fig. 30, Plate LIII). It was also noted that the indications in the lower-zinc brasses tended to be centrally located and to taper off in width towards the grain boundary (Figs. 24 and 26, Plate LII) rather than to be confined to the grain- and twin-boundary areas.

The 97 : 3 brasses showed a transition series of microstructures. The electrolytic thiosulphate etch developed the normal Type I indications at low deformations at approximately the same sensitivity as in the 90 : 10 brass (see Fig. 4). Type III indications similar to, but not as prominent as, those found in copper began to be developed at about 30% compression, and had completely replaced the Type I by 40% compression (Fig. 25, Plate LII). The grain-count curve flattened off with the development of Type III indications in a similar manner to that found for copper (cf. Figs. 1 and 3). At 50% compression, however, the broad Type II indications characteristic of the higher-zinc brasses appeared and developed rapidly as the Type III indications disappeared (Fig. 26, Plate LII). The distinction between the Types II and III indications was not, however, at all clear at the intermediate deformations. The grain count increased sharply to 100% with the introduction of Type II indications (Fig. 3).

The majority of the remaining etching techniques developed both Types II and III indications in this brass, a typical grain-count curve being shown in Fig. 3; the sensitivity for detecting deformation was very low, which is responsible for the sharp maximum in the upper curve of Fig. 4. Exceptions were the

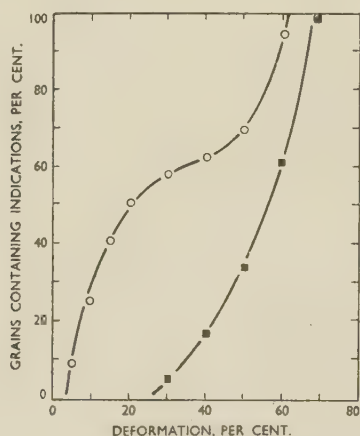


FIG. 3.—Grain Counts of Indications Developed in 97 : 3 Brass.

KEY.
○ Electrolytic thiosulphate etch (Types I, III, and II).
■ Ferric chloride etch (Types III and II).

potassium dichromate and ammonium hydroxide-hydrogen peroxide reagents, which developed confusing etch facets and were unsuitable for examining this alloy. This probably accounts for the fact that Hibbard *et al.*,⁶ who used the potassium dichromate

reagent, did not report a maximum in their corresponding sensitivity curve.

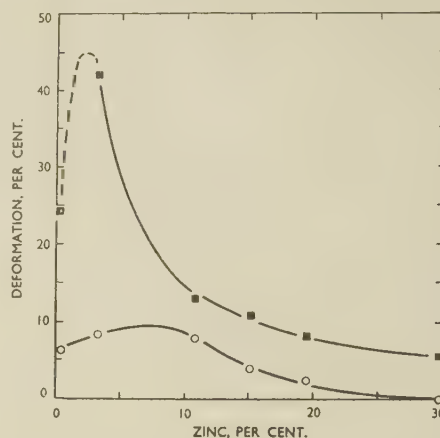


FIG. 4.—Effect of Zinc Content on Deformation Required to Develop Indications in 20% of the Grains.

KEY.
○ Electrolytic thiosulphate etch (Type I).
■ Ferric chloride etch (Types II and III).

IV.—THE NATURE OF THE INDICATIONS

1. TYPE I INDICATIONS

Although there can be little doubt from previous work, particularly that of Burke and Barrett,³ that the indications develop at traces of (111) planes, it has not yet been proved conclusively that they develop at the sites of operative slip planes (see Hibbard's¹⁵ discussion on Burke and Barrett³). It was thought that more conclusive evidence on this point might be obtained from the examination of taper sections of deformed surfaces.

Specimens of annealed 70 : 30 brass were prepared metallographically by the method outlined in Section II, 2, and were lightly deformed by cold hammering to produce slip lines on the polished surface. Since it is known that this surface originally was essentially free from deformation (no Type I indications could be developed under the most sensitive etching conditions), it can be assumed that the true slip structure has been developed (Brown and Honeycombe¹⁶). The surface was then heavily copper-plated, taper-sectioned at a nominal taper ratio of 10 : 1, prepared metallographically, and etched to develop Type I indications. Direct evidence was obtained at a number of positions that the etching indications were associated with the classical slip steps at the deformed surface (Fig. 29, Plate LIII).

It is suggested, therefore, that these features might be called "slip-line indications". The term distinguishes the etching effects from the basic phenomenon with which they are associated, and from the Type II indications discussed below.

2. TYPE II INDICATIONS

It is clear from the metallographic evidence that this type is closely related to, and a development of,

the slip-line indications. It is reasonable to expect, therefore, that they represent some modification of the slip process.

If a polished surface of 70 : 30 brass was deformed as above, the normal fine, uniformly spaced slip lines were developed on the surface at low deformations. At about 10% compression, however, dark-shadowed bands could be observed amongst the slip lines when the surface was viewed under oblique illumination (Fig. 27, Plate LII), suggesting that slip was now tending to occur preferentially at these local areas. The bands extended from the grain and twin boundaries, as do the Type II indications. This phenomenon could be observed with more clarity in a 90 : 10 brass, when the bands were first detected at about 20% compression, were broader and more widely spaced, and formed first in the central areas of the grains (Fig. 28, Plate LII); the general form of the bands was again very similar to the Type II indications etched in corresponding sections (cf. Figs. 24 and 28, Plate LII). Examination at high magnification showed that the areas adjoining the bands were both relatively flat, although at slightly different levels; the bands themselves could be resolved into a series of very closely spaced, individual slip lines as the focus was raised from one level to the other.

It would appear, therefore, that the bands are steps in the surface at which relatively large amounts of deformation have occurred on a number of closely adjacent slip planes. The evidence also suggested that the development of these bands of multiple lamellar slip is responsible for the Type II indications in corresponding sections. This interpretation was confirmed by the examination of taper sections of deformed surfaces of specimens of 90 : 10 brass; a series of marked local steps was then observed at the surface, a Type II indication being etched at the site of each step (Fig. 30, Plate LIII). Individual slip steps were also evident between each major step, and each of these presumably would have been associated with a slip-line indication under suitable etching conditions.

It is suggested, therefore, that, at an early stage in the deformation of polycrystalline brasses, a change in the deformation process occurs whereby slip tends to take place preferentially in localized groups of slip planes constituting a lamellar slip band, rather than on a series of uniformly and closely spaced single slip lines throughout the crystal; the sites of the lamellar band etch strongly, giving rise to the Type II indications. This interpretation of the indications fully conforms with the metallographic observations. The characteristics of the metallographic indications do not, however, necessarily reflect quantitatively the nature of the slip bands. For example, the first development of the indications presumably lags somewhat behind the initiation of lamellar slip. The width of the indications and their progressive development at higher deformations do seem, however, to be true characteristics of the bands. The present examination also suggests that the location of the indications

is a true characteristic of the bands. The indications might well be termed "slip-band indications".

Fig. 30 (Plate LIII) shows that a structure in the covering electrodeposit is associated with each multiple slip band. This structure is thought to result from the reproduction in the electrodeposit of the difference in orientation developed between the heavily deformed slip-band areas and the more lightly deformed intermediate areas. This matter will be discussed in a future publication.

3. TYPE III INDICATIONS

No conclusive information has been obtained as to the nature of Type III indications, but it is likely that they also are associated with an inhomogeneity in the deformation process. Hibbard,¹⁷ who described similar etching indications in copper, also ascribed them to inhomogeneous deformation resulting in measurable differences in crystal orientations within a single grain. The distortion of the sub-grain structure of deformed copper observed by Delisle¹⁸ may be evidence of this, but her work was not extensive enough to enable a satisfactory comparison to be made.

4. TYPE IV INDICATIONS

The nature of Type IV indications was not investigated. It seems to be agreed that they are associated with the formation of deformation bands (Barrett and Steadman,¹⁹ and Barrett²⁰), and it is therefore suggested that they be termed "deformation-band indications".

VI.—SUMMARY AND DISCUSSION

The examination has established that several distinct metallographic indications of deformation can be developed in copper and α -brasses. So far as the detection of relatively low deformations is concerned, the two important types of indication are as follows:

Slip-Line Indications.—Indications which are developed as systems of lines, grooves, or etch pits and which are associated with (optically) single operative slip planes. They are developed by the electrolytic thiosulphate etch in the whole series of alloys investigated, and by a limited number of other etching methods in higher-zinc brasses. The sensitivity of development is particularly high in 70 : 30 brasses, strains of <0.1% compression being detected readily. Whether or not these indications are developed simultaneously with the first traces of slip will be discussed in a future publication.

Slip-Band Indications.—Indications which are developed easily in the α -brasses by all etching methods. They usually appear as relatively broad bands, and are thought to be associated with a change in the deformation process whereby slip tends to occur inhomogeneously in bands of lamellar slip.

The new information, particularly the inability of many etching techniques to develop slip-line indications, satisfactorily explains most of the divergent

results reported by previous investigators. Burke and Barrett³ used a high-sensitivity etch for their investigation on 70:30 brass, but apparently did not distinguish between the two types of indications. Jacquet's^{7,8} technique, if used under suitable conditions, develops the slip-line indications in 70:30 brass with very high sensitivity, and Jacquet also made some distinction between the two types of indications. Brick,¹ Brick and Williamson,² Cook and Richards,⁴ and Hibbard *et al.*,⁶ in their investigations of 70:30 brasses, used etching techniques which develop slip-band indications only, and consequently a relatively low sensitivity was obtained. The majority of McLean's⁵ results are also in this category.

There is a further possible cause of discrepancies in the results of investigators who detected slip-band indications only. The development of these indications follows upon a change from a homogeneous to an inhomogeneous slip process, and it is possible that the strain at which this change occurs may depend upon the method of deformation. The indications detected in copper by Cook and Richards^{9,10} were deformation-band indications; these investigators apparently failed to detect the Type III indications. The suitability of Jacquet's¹¹ short-circuit etch for detecting deformation in copper was not confirmed.

The results obtained with the high-zinc α -brasses suggest that in these alloys the metallographic method may be of general usefulness for the investigation of inhomogeneities of deformation within the body of a specimen, and for determining the presence and extent of areas of local deformation. Even the information so far obtained has some general application to the theory of deformation of metals. Particular points are the conclusions that coarse multiple slip bands do develop in high-zinc α -brasses, that the formation of the multiple bands is preceded by uniform fine single slip, and that the latter slip is not confined to the surface layers but occurs throughout the body of the material.

Slip-band lamellae have previously been observed on a somewhat coarser scale in single crystals of α -brasses by Treuting and Brick²¹ and by Maddin, Mathewson, and Hibbard.^{22,23} Kuhlmann-Wilsdorf and Wilsdorf,²⁴ however, failed to detect any evidence of slip bands by electron-microscope examination of polycrystalline 70:30 brass, and they attributed the observations of Treuting and Brick²¹ to "geometrical softening". The present work strongly suggests that slip-band lamellae are a real feature of the deformation process of α -brasses. It is to be noted that the scale of the slip bands proposed here would cover several fields of view at the magnifications used by the Wilsdorfs, and it is possible that the structure escaped their observation.

Slip-band lamellae have also been observed in aluminium,²⁴⁻³⁰ nickel, lead, and magnesium,³¹ and copper and silver.²⁴ In all these metals, the bands appeared as single lines under the optical microscope and were resolved only by critical examination with the electron microscope. It might be thought, there-

fore, that those slip lines in the α -brasses referred to here as "single" lines could be resolved into lamellar bands by the electron microscope. The work of Kuhlmann-Wilsdorf and Wilsdorf²⁴ indicates, however, that this is not so; Brown³² comes to the same conclusion in reviewing the work of Maddin *et al.*^{22,23}

Two opposing views are held as to the nature of the slip process in the regions between the lamellar bands. Kuhlmann-Wilsdorf and Wilsdorf²⁴ conclude that the earliest deformation occurs on fine uniformly spaced lines, which they term "elementary" slip, and that the lamellar bands develop amongst these at a later stage of deformation. This view is in accord with the observations of Andrade and Roscoe,³³ who worked with cadmium single crystals, and Brown³² independently arrived at the same conclusion as an alternative explanation of the formation of the "micro-slip" observed by Brown and Honeycombe.¹⁶ As discussed above, the present investigation suggests that the deformation of α -brasses occurs in a similar manner.

On the other hand, the remaining investigators of slip bands did not observe any slip in the inter-band regions at low deformations; as a result, it has been concluded that deformation starts at, and is essentially confined to, the slip bands which spread laterally as deformation proceeds.^{26,32} A number of the observations responsible for this conclusion were carried out on specimens which had been mechanically abraded and electrolytically polished.²¹⁻²³ It is quite possible that such surfaces contained residual surface deformation, in which case the work of Brown and Honeycombe¹⁶ adequately explains the suppression of elementary slip in the inter-band regions. Further, electrolytically polished surfaces may be covered with a thin oxide film which prevents the development of elementary slip lines. This is particularly likely in the case of aluminium, where the thickness of the oxide film depends greatly on the exact method of preparation of the specimen (Raether³⁴), and may account for the failure of Heidenreich and Shockley,^{25,26} and of Brown,²⁷⁻²⁹ to observe the elementary slip.

Even admitting that the elementary slip precedes the formation of lamellar slip bands, the question remains as to whether it is truly representative of the method of deformation in the body of the material or whether it is merely a surface phenomenon. Brown³² has reviewed the previously available evidence and favours the former view. Kuhlmann-Wilsdorf *et al.*,³⁵ after a similar review and a theoretical discussion which suggests that the sources of dislocations may well lie at the surface, conclude that the latter may be true. Both reviews, however, indicate that the available evidence is far from conclusive, mainly because previous investigations have necessarily been confined to the surface itself. The present metallographic methods for the first time permit some assessment to be made of this question, since the detection of slip-line indications in the interior of deformed material would appear to be direct evidence

that elementary slip is a true feature of the deformation process in α -brasses. It will also be seen in Fig. 29 (Plate LIII), that the slip-line indications show no diminution in intensity with increasing depth, whereas Kuhlmann-Wilsdorf *et al.*³⁵ in their discussion assumed that the contrary is true.

Whether or not the information obtained in this investigation is applicable to other metals depends, of course, on the completeness of the analogy between the respective slip processes. It is suggested that there is a distinct possibility that a reasonable analogy does exist, the main difference being that the phenomena are on a sufficiently coarse scale in α -brasses to be resolved by the optical microscope. If it is accepted that Kuhlmann-Wilsdorf and Wilsdorf²⁴ overlooked any coarse lamellar slip bands in the α -brass specimens examined, the remainder of their work is in agreement with this suggestion, since the finest slip observed by them in α -brass was considerably coarser than the finest slip observed in the pure metals, the proportionate scale between the two cases being of the order suggested here. On the present view, the finest slip in α -brass might be regarded as the comparable "elementary" slip structure, and this is the sense in which the term has been used above.

The above discussion applies specifically to medium- and high-zinc α -brasses. The characteristics of the metallographic indications developed in pure copper are of quite a different order. The etching effects referred to as Type I indications in this material cannot result from the elementary slip structure found by Kuhlmann-Wilsdorf and Wilsdorf²⁴ in pure copper, but are more likely to be related to the fine slip lamellae observed by them. The relationship between the metallographic indications and the respective deformation processes in both copper and low-zinc α -brasses requires further elucidation. If this were forthcoming, the metallographic method might be of value in investigating the deformation processes of the pure metal. Further, it would seem desirable to extend the work of Kuhlmann-Wilsdorf and Wilsdorf²⁴ to the examination of a complete range of brasses.

The new observations also indicate that some reconsideration of current explanations as to why the indications develop is necessary. The etch-pit nature of many of the indications, the differential colouring effects produced by the sensitive electrolytic thio-sulphate etch, and the ease of developing slip-band indications compared with slip-line indications all support the suggestion that the indications are due to selective etching of a strained region associated with the slip lines. Kuhlmann-Wilsdorf and Wilsdorf²⁴ have suggested that the differential etching occurs because the slip areas are thermodynamically unstable owing to the presence of piled-up dislocations. They suggested that indications are not developed in pure metals because the slip is much finer and hence the dislocation density is more uniform. It has been shown here that etch-pit indications are developed in copper, but this is not inconsistent with the Wilsdorfs' explanation if it is assumed that these indications

develop at the relatively widely spaced lamellar slip bands. Gilman³⁶ has adapted Fisher's³⁷ suggestion that slip in an alloy changes the short-range order pattern across the slip plane, pointing out that this would change the chemical potential. This explanation, however, cannot account for the development of indications in copper.

Amelinckx³⁸ suggests that the etch pits develop at points where screw dislocations emerge at the surface along the slip line, and Jacquet³⁹ has advanced a similar explanation for the etch pits which can be developed in brass (as in Fig. 13, Plate LI). Even if this were so, some additional etching mechanism must be proposed to account for the fact that slight alterations in etching conditions cause the etch pits in brass to be replaced by continuous lines (as in Fig. 12, Plate L). A further difficulty encountered by all these theories is in explaining why high sensitivity in detecting deformation is restricted to certain alloy groups and, more particularly, why the sensitivity in the α -brasses changes so markedly when the zinc content decreases from 30 to 20%. Perhaps a really satisfactory theory is not to be expected when so little fundamental information is available as to the mechanism of the simplest etching processes.

APPENDIX

TABLE IV.—*Etching Techniques.*

Etching Method	Conditions of Use	Used by Previous Investigators
Potassium dichromate reagent	Potassium dichromate 5 g. Sulphuric acid (conc.) 8 ml. Water 50 ml. Hydrochloric acid (conc.) 2 ml./50 ml. Apply by swabbing.	Hibbard, <i>et al.</i> ⁶
Ammonium hydroxide-hydrogen peroxide reagent	Ammonium hydroxide 1 vol. Hydrogen peroxide (3%) 2 vol. Water 2 vol. Apply by swabbing.	Burke and Barrett ³
Ferric chloride reagent	Ferric chloride 5 g. Hydrochloric acid (conc.) 10 ml. Water 100 ml. Etch by immersion.	
Phosphoric acid reagent	10% solution at 90° C.; etch by immersion.	McLean ⁶
Ammonium persulphate reagent	10% solution at 50°–60° C.; etch by immersion.	
Cupric ammonium chloride reagent *	10% solution to which concentrated ammonia is added until definitely alkaline.	McLean ⁶
Electrolytic short-circuit etch †	Electrodes of standard electropolishing bath short-circuited at end of polishing cycle.	Jacquet ¹¹
Electrolytic polishing cell etch	Washed and dried specimen immersed in standard orthophosphoric acid polishing bath at 0.6–0.8 V.	
Electrolytic thio-sulphate etch ‡: High-sensitivity etch Low-sensitivity etch	0.25% solution at 3.5 amp./dm. ² 0.5% solution at 1 amp./dm. ²	Jacquet ^{7, 8}

* Neutral solutions do not develop Type I indications.

† Fresh phosphoric acid solutions produced etch facets, as described by Jacquet.¹¹ ‡ Used solutions containing copper ions re-deposit copper, as described by Crussard *et al.*⁴⁰

§ In order to obtain the high-sensitivity etch with high-zinc brasses, extreme precautions against contamination of the bath with phosphoric acid are necessary. In copper and low-zinc brasses, the etch film is not stable and must be protected immediately with a clear lacquer.

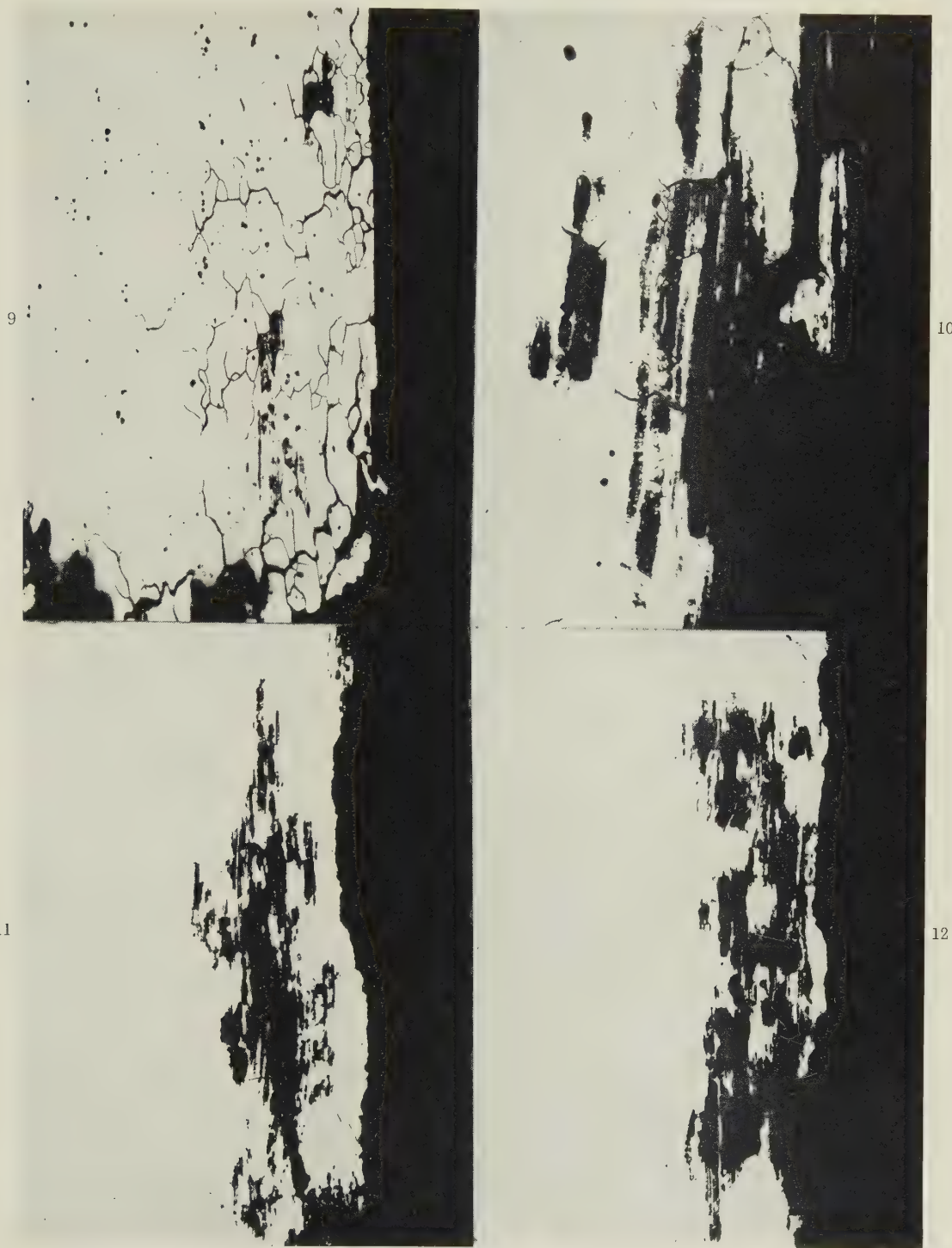
ACKNOWLEDGEMENT

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REFERENCES

1. R. M. Brick, *Trans. Amer. Inst. Min. Met. Eng.*, 1940, **137**, 193.
2. R. M. Brick and M. A. Williamson, *ibid.*, 1941, **143**, 84.
3. J. E. Burke and C. S. Barrett, *ibid.*, 1948, **175**, 106.
4. M. Cook and T. Ll. Richards, *J. Inst. Metals*, 1943, **69**, 351.
5. D. McLean, *ibid.*, 1948, **74**, 95.
6. W. R. Hibbard, Jr., R. W. Fenn, Jr., H. Margolin, and H. P. Moore, *Trans. Amer. Inst. Min. Met. Eng.*, 1948, **175**, 74.
7. P. A. Jacquet, *Compt. rend.*, 1949, **228**, 1027.
8. P. A. Jacquet, *Rev. Mét.*, 1950, **47**, 355.
9. M. Cook and T. Ll. Richards, *J. Inst. Metals*, 1940, **66**, 1.
10. M. Cook and T. Ll. Richards, *ibid.*, 1941, **67**, 203.
11. P. A. Jacquet, *Rev. Mét.*, 1945, **42**, 133.
12. L. E. Samuels, *J. Inst. Metals*, 1952-53, **81**, 471.
13. E. C. W. Perryman and Mary Lack, *Metallurgia*, 1951, **44**, 97.
14. D. McLean, private communication.
15. W. R. Hibbard, Jr., *Trans. Amer. Inst. Min. Met. Eng.*, 1948, **175**, 123 (discussion on Burke and Barrett³).
16. A. F. Brown and R. W. K. Honeycombe, *Phil. Mag.*, 1951, [vii], **42**, 1146.
17. W. R. Hibbard, Jr., *Trans. Amer. Inst. Min. Met. Eng.*, 1949, **180**, 52.
18. L. Delisle, *ibid.*, 1953, **197**, 660.
19. C. S. Barrett and F. W. Steadman, *ibid.*, 1942, **147**, 57.
20. C. S. Barrett, "Structure of Metals: Crystallographic Methods, Principles and Data". 1952: New York (McGraw-Hill Book Co., Inc.); London (McGraw-Hill Publishing Co., Ltd.)
21. R. B. Treuting and R. M. Brick, *Trans. Amer. Inst. Min. Met. Eng.*, 1942, **147**, 128.
22. R. Maddin, C. H. Mathewson, and W. R. Hibbard, Jr., *ibid.*, 1948, **175**, 86.
23. R. Maddin, C. H. Mathewson, and W. R. Hibbard, Jr., *ibid.*, 1949, **185**, 527.
24. D. Kuhlmann-Wilsdorf and H. Wilsdorf, *Acta Met.*, 1953, **1**, 394.
25. R. D. Heidenreich and W. Shockley, *J. Appl. Physics.*, 1947, **18**, 1029.
26. R. D. Heidenreich and W. Shockley, *Phys. Soc.: Rep. Conf. on Strength of Solids*, 1948, p. 57.
27. A. F. Brown, *Nature*, 1949, **163**, 961.
28. A. F. Brown, *Metallurgical Applications of the Electron Microscope* (*Inst. Metals Monograph No. 8*), 1950, 103.
29. A. F. Brown, *J. Inst. Metals*, 1951-52, **80**, 115.
30. R. I. Garrod, J. W. Suiter, and W. A. Wood, *Phil. Mag.*, 1952, [vii], **43**, 677.
31. R. D. Heidenreich, *Rev. Sci. Instruments*, 1952, **23**, 583.
32. A. F. Brown, *Advances in Physics*, 1952, **1**, 427.
33. E. N. da C. Andrade and R. Roscoe, *Proc. Phys. Soc.*, 1937, **49**, 152.
34. H. Raether, *Métaux et Corrosion*, 1950, **25**, 1.
35. D. Kuhlmann-Wilsdorf, J. H. van der Merwe, and H. Wilsdorf, *Phil. Mag.*, 1952, [vii], **43**, 632.
36. J. J. Gilman, *Acta Met.*, 1953, **1**, 764.
37. J. C. Fisher, *ibid.*, 1954, **2**, 9.
38. S. Amelinckx, *Phil. Mag.*, 1953, [vii], **44**, 1048.
39. P. A. Jacquet, *Compt. rend.*, 1953, **237**, 1248.
40. C. Crussard, F. Aubertin, B. Jaoul, and G. Wyon, "Progress in Metal Physics" (Edited by B. Chalmers), Vol. 2, p. 193. 1950: London (Butterworths Scientific Publications).

MICROSTRUCTURES OF ALUMINIUM-COPPER AND ALUMINIUM-COPPER-CADMIUM ALLOYS AFTER STRESS-CORROSION.



FIGS. 9 and 11.—Al-41% Cu. (Alloy FY.)

FIGS. 10 and 12.—Al 41% Cu-0.1% Cd. (Alloy FZ.)

FIG. 9.—Aged for 16 hr. at 165° C., failed after 10 days at 12.4 tons/in.². × 100.FIG. 10.—Aged for 6 hr. at 185° C., unbroken after 187 days at 21.9 tons/in.². × 250.FIGS. 11 and 12.—Aged for 3 hr. at 170° C., rolled to 10% reduction, aged for 9 hr. at 165° C., unbroken after 200 days at 23 tons/in.². × 100.

MICROSTRUCTURES OF NICKEL-FREE ALUMINIUM BRONZE (ALLOY 2).

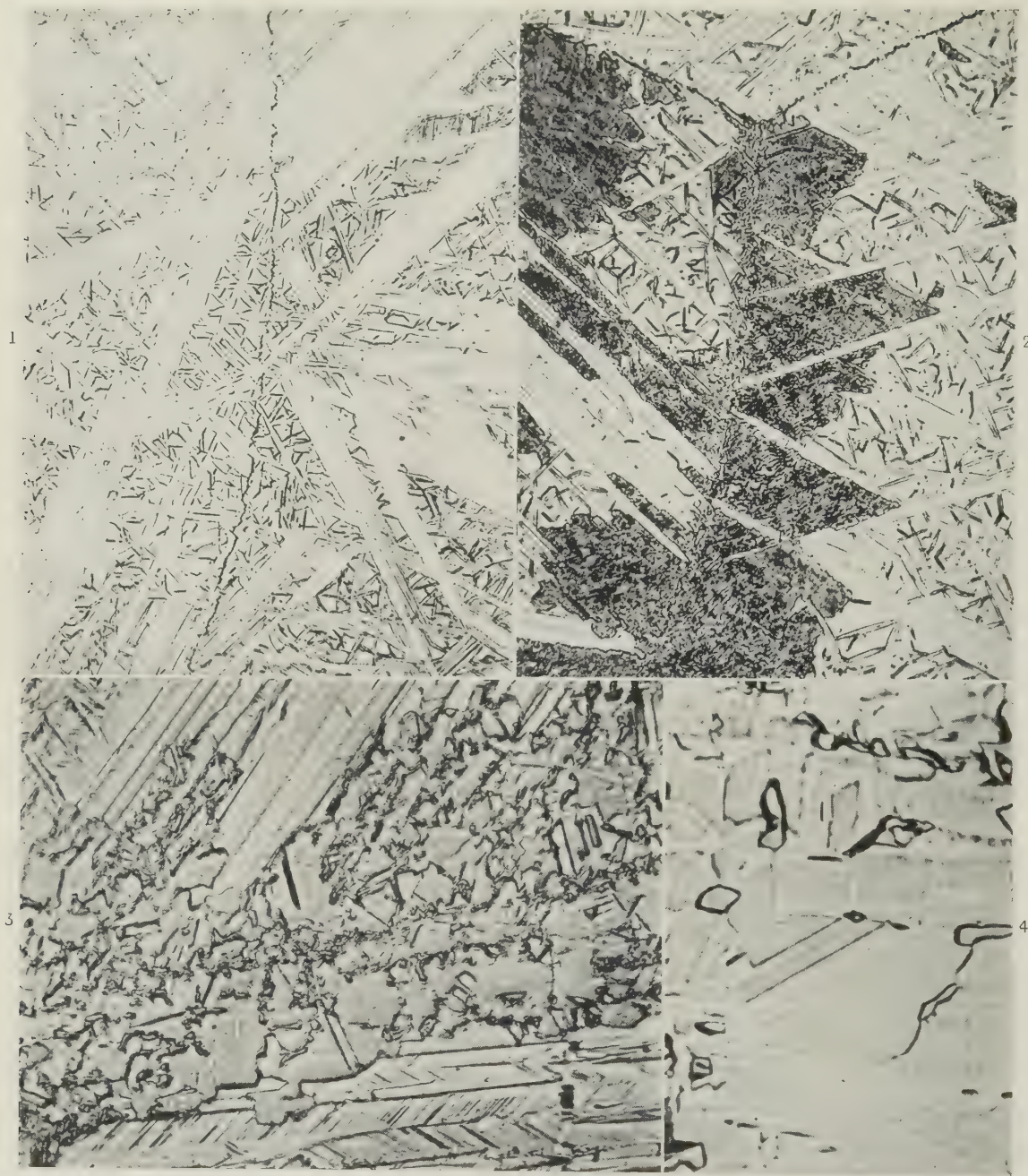


FIG. 1.—Transformed for 68 Min. at 378° C. α Precipitate is in the grain boundary. Fine needles are present in certain parts of the acicular structure. $\times 230$.

FIG. 2.—Transformed for About 2 Days at 378° C. Transformation of " β " to eutectoid, which is growing most quickly in parts containing fine needles. $\times 230$.

Etched in aqueous chromic acid solution.

FIG. 3.—Transformed for 5 Weeks at 350° C. Duplex grain-boundary precipitate in a matrix of " β ". $\times 600$.

FIG. 4.—Transformed for 5 Weeks at 350° C. Duplex constituent showing twinning in matrix phase. $\times 1600$.

Etched in ammonia and hydrogen peroxide.

MICROSTRUCTURES OF ALUMINIUM BRONZES CONTAINING NICKEL.

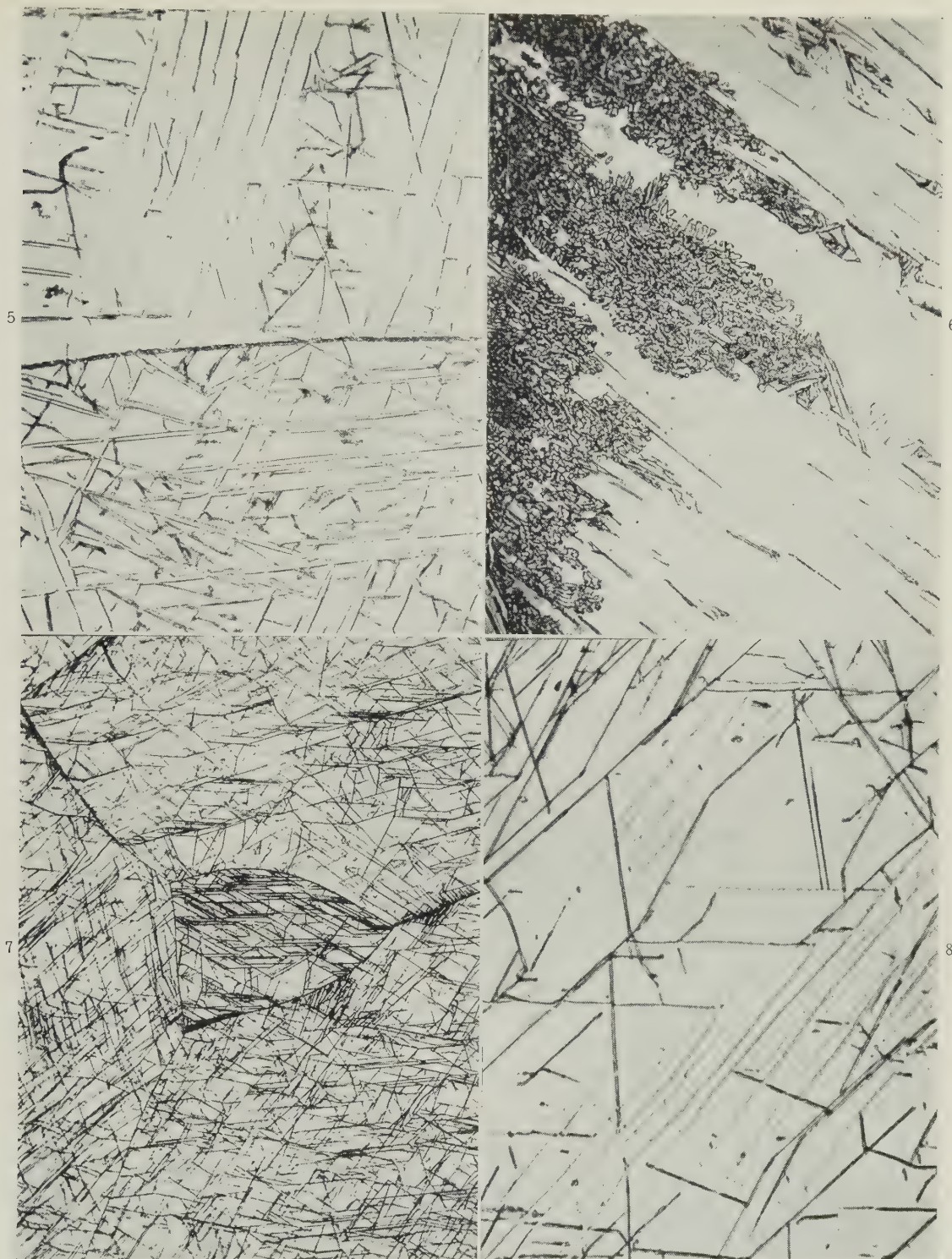


FIG. 5.—Alloy 4 Transformed for 2½ Hr. at 373° C. Grain-boundary α and " β ", which is composed of coarse acicular constituent and long thin needles. $\times 600$.

FIG. 6.—Alloy 4 Transformed for 3 Weeks at 350° C. Non-lamellar eutectoid is growing preferentially in certain parts of the " β ". $\times 600$.

FIG. 7.—Alloy 6 Transformed for 5 Min. at 350° C. Long fine needles are present in the " β ". $\times 150$.

FIG. 8.—Alloy 6 Transformed for 5 Min. at 350° C. The structure consists of a coarse acicular constituent and long fine needles. $\times 850$.

Etched in aqueous chromic acid solution.

MICROSTRUCTURES OF ALUMINIUM BRONZES CONTAINING NICKEL (ALLOY 6).

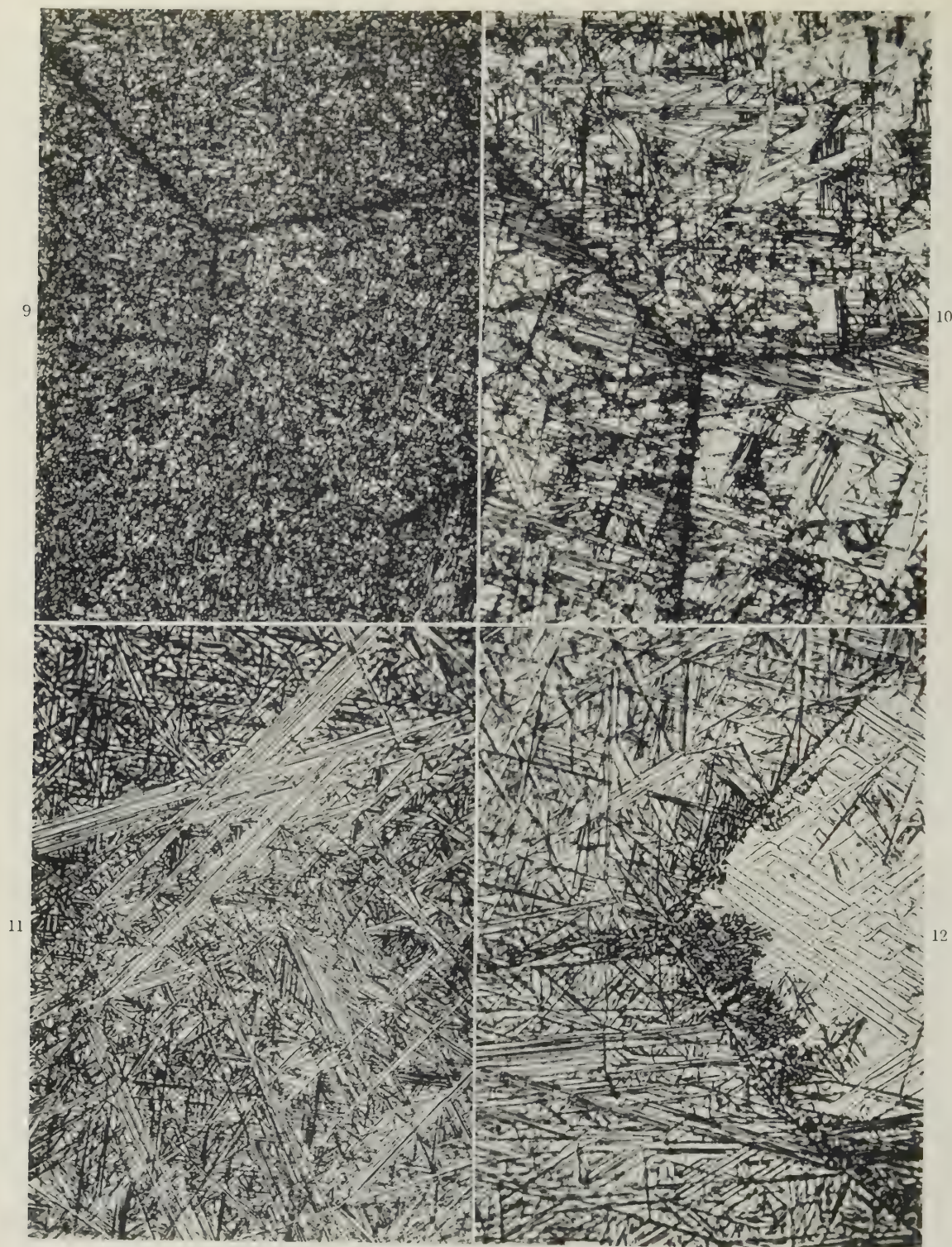


FIG. 9.—Transformed for 15 Min. at 350° C. The long fine needles in the " β " are very numerous. $\times 150$.

FIG. 10.—Transformed for 15 Min. at 350° C. The structure is a very intimate mixture of fine needles and a coarser acicular constituent. $\times 600$.

FIG. 11.—Transformed for 1 Hr. at 350° C. The coarser acicular constituent is more clearly defined than in specimens transformed for shorter periods and many fine needles are present. $\times 600$.

FIG. 12.—Transformed for 1 Day at 350° C. Eutectoid is forming at grain boundaries and grows preferentially in one constituent of the " β ". $\times 600$.

Etched in aqueous chromic acid solution.

MICROSTRUCTURES OF COMPRESSED COPPER AND BRASS. $\times 500$.

FIGS. 5-8.—Tough-Pitch Copper. Electrolytic thiosulphate etch.
 FIG. 5.—2.5% compression (Type I).
 FIG. 6.—20% compression (Type I).
 FIG. 7.—40% compression (Type III).
 FIG. 8.—50% compression (Type III).
 FIGS. 9-10.—Tough-Pitch Copper. Potassium dichromate etch. Oblique illumination.
 FIG. 9.—40% compression (Type III).
 FIG. 10.—70% compression (Type IV).
 FIGS. 11-12.—70 : 30 Brass. High-sensitivity electrolytic thiosulphate etch.
 FIG. 11.—Annealed.
 FIG. 12.—0.1% compression (Type I).

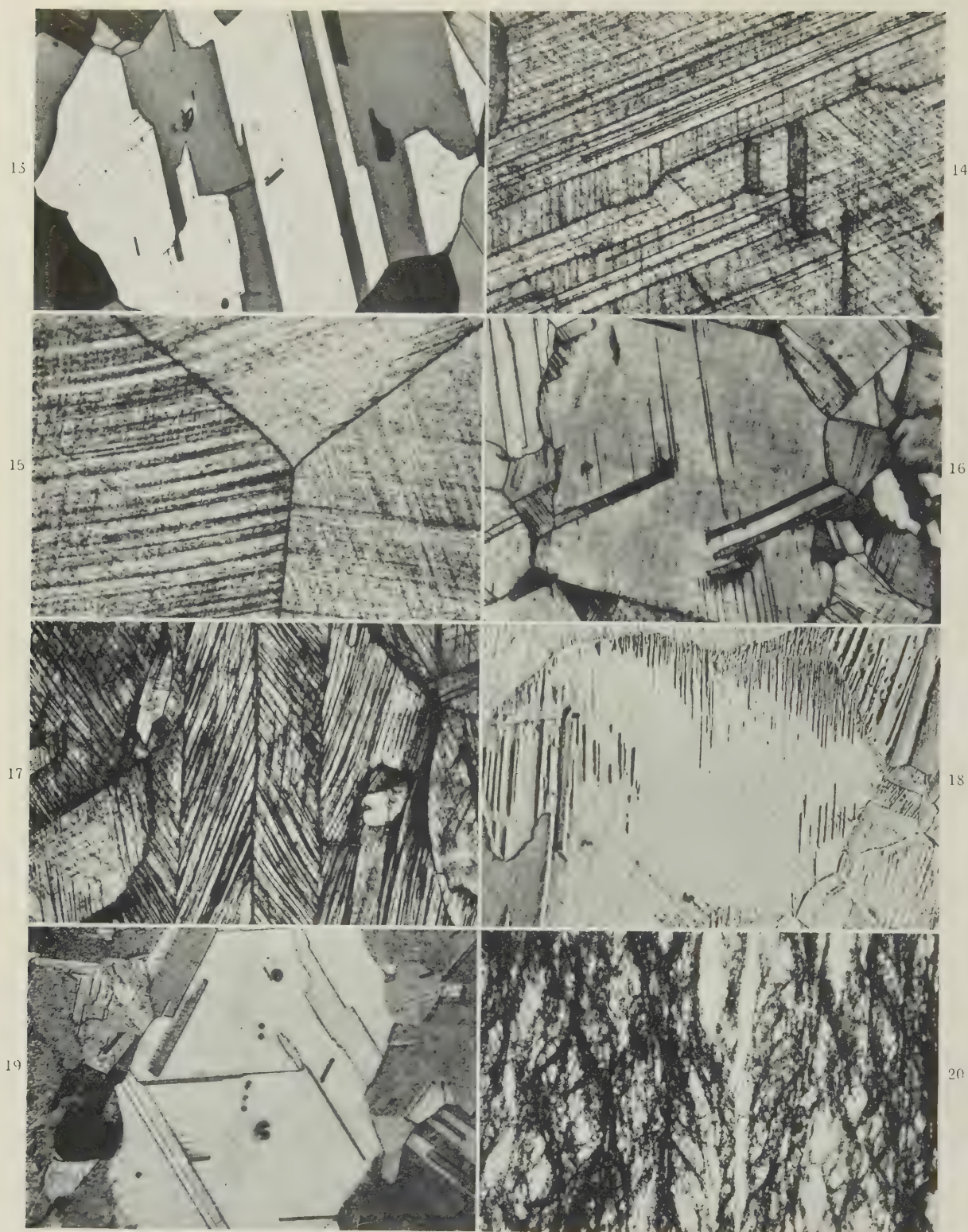
MICROSTRUCTURES OF COMPRESSED 70 : 30 BRASS. $\times 500$.

FIG. 13.—0.1% Compression. Low-sensitivity electrolytic thiosulphate etch (Type I).
 FIG. 14.—2.5% Compression. High-sensitivity electrolytic thiosulphate etch (Type I).
 FIG. 15.—5% Compression. High-sensitivity electrolytic thiosulphate etch (Type I).
 FIG. 16.—10% Compression. Low-sensitivity electrolytic thiosulphate etch (Types I and II).
 FIG. 17.—20% Compression. Low-sensitivity electrolytic thiosulphate etch (Type II).
 FIG. 18.—10% Compression. Ammonium hydroxide etch (Types I and II).
 FIG. 19.—0.8% Compression. Electrolytic polishing cell etch (Type I).
 FIG. 20.—80% Compression. Ammonium hydroxide etch (Type IV).

MICROSTRUCTURES OF COMPRESSED BRASSES

500

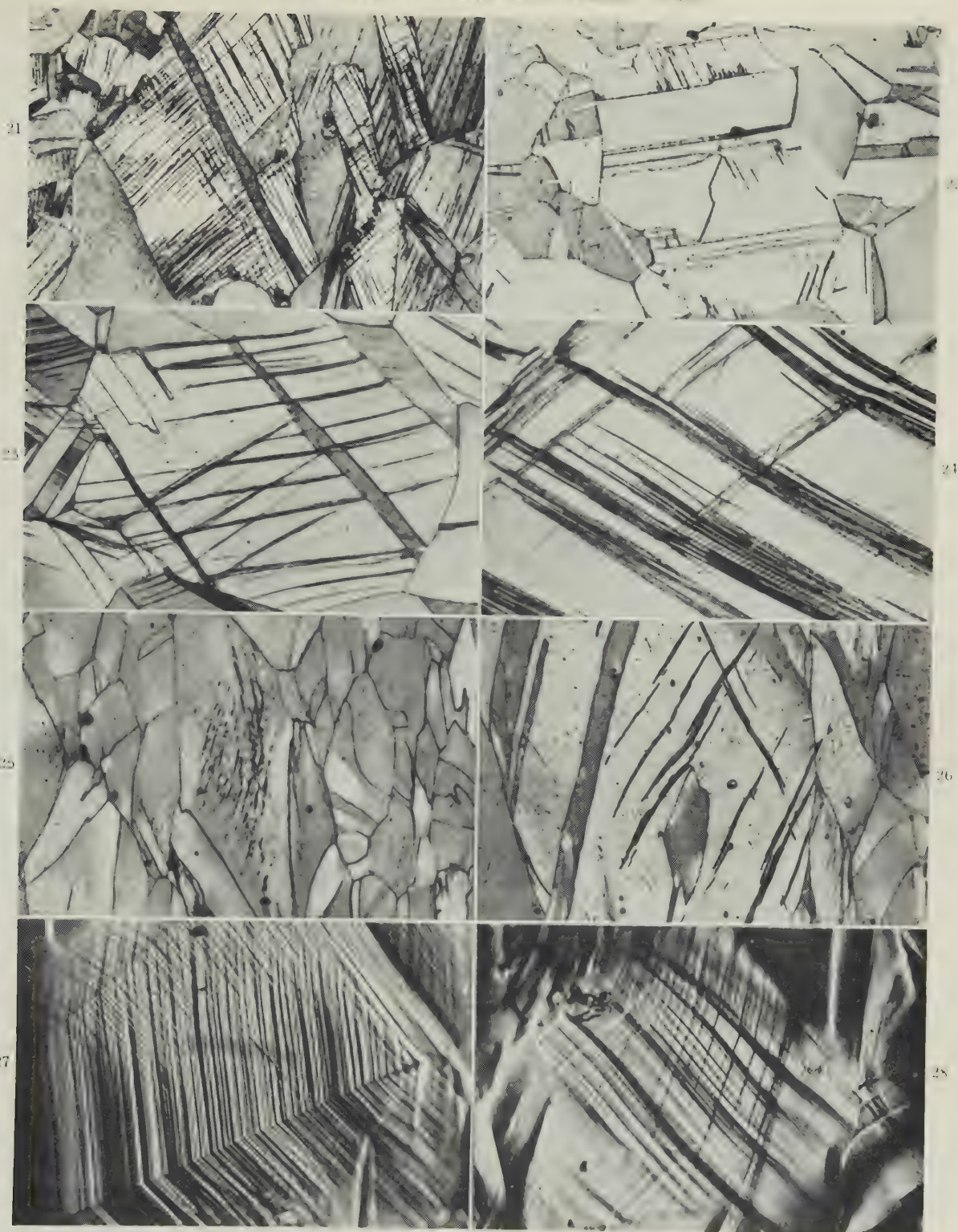
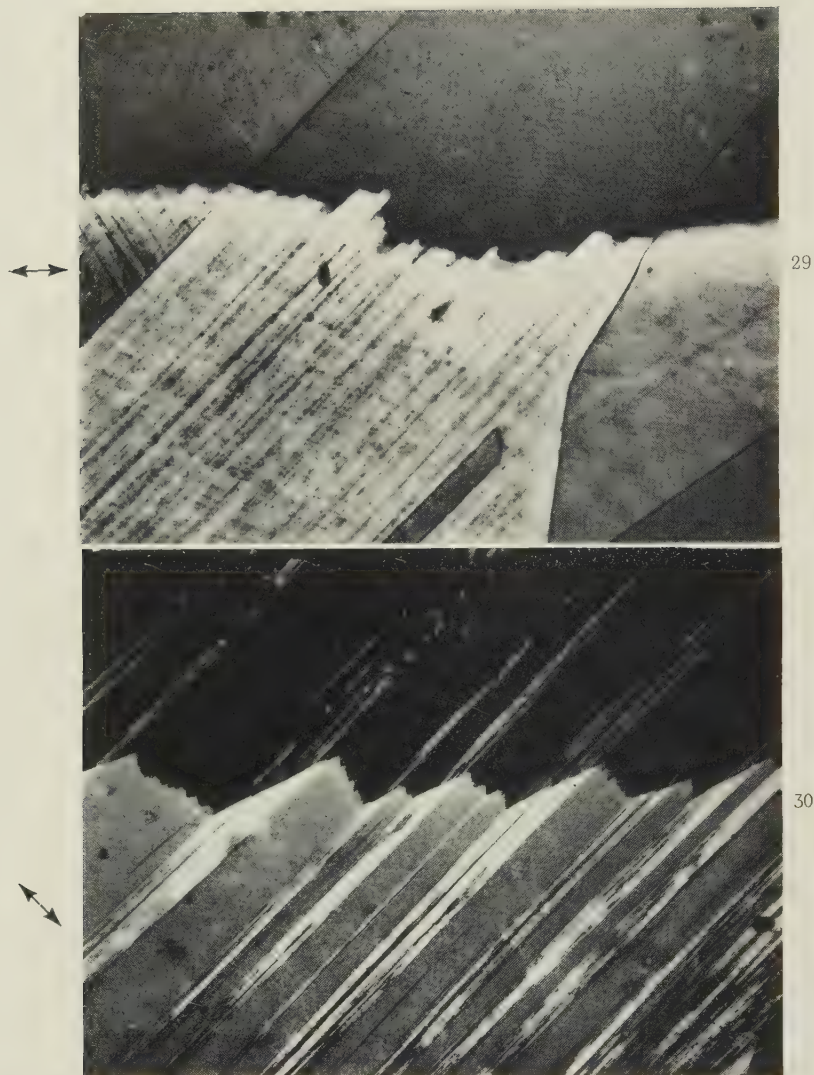


FIG. 21.—70 : 30 Brass. 20% compression. Ferric chloride etch (Type II).
 FIG. 22.—70 : 30 Brass. 5% compression. Phosphoric acid etch (Type II).
 FIG. 23.—85 : 15 Brass. 20% compression. Electrolytic thiosulphate etch (Type II).
 FIG. 24.—70 : 10 Brass. 20% compression. Ferric chloride etch (Type II).
 FIG. 25.—97 : 3 Brass. 40% compression. Electrolytic thiosulphate etch (Type III).
 FIG. 26.—97 : 3 Brass. 60% compression. Electrolytic thiosulphate etch (Type II).
 FIG. 27.—70 : 30 Brass. Surface after 10% compression. Oblique illumination.
 FIG. 28.—90 : 10 Brass. Surface after 20% compression. Oblique illumination.



FIGS. 29 and 30.—Taper Sections of Deformed Brass Surfaces.

FIG. 29.—70 : 30 Brass. 5% compression. Electrolytic thiosulphate etch (Type I).

FIG. 30.—90 : 10 Brass. 20% compression. Ferric chloride etch (Type II).

Horizontal mag. $\times 500$; Taper ratio 10 : 1.

The approximate direction of the traces of the surface before deformation is indicated at the sides of the figures.

INTERCRYSTALLINE FRACTURE OF BETA-BRASSES CONTAINING ALUMINIUM *

1606

By E. C. W. PERRYMAN,† M.A., A.I.M., MEMBER

(Communication from The British Non-Ferrous Metals Research Association.)

SYNOPSIS

Earlier work has shown that cast β -brasses containing 3% or more of aluminium are susceptible to delayed intercrystalline fracture when loaded in sodium chloride solution, in air, or in inert liquids (Bailey, *Metal Ind.*, 1952, **80**, 519). A possible explanation is that relaxation of shear stress along appropriately oriented grain boundaries results in the establishment of stress concentrations at other boundaries, with consequent formation of intercrystalline cracks.

The purpose of the work described is, first, to show that intergranular failures occurring in binary and ternary β -brasses are probably due to a mechanism of this kind, and, secondly, to provide some evidence that the effects of aluminium may, at least in part, be exercised through some modification of the grain-boundary structures.

I.—INTRODUCTION

It has been shown by Bailey¹ that cast β -brasses containing 3% or more of aluminium, when stressed at the 0.1% proof stress in 3% sodium chloride solution, in air, or in inert liquids, such as paraffin, are susceptible to delayed intercrystalline fracture. Alloys containing less than 3% aluminium either did not fail in 40 days or broke with a transcrystalline fracture. An alloy containing 4% aluminium was more susceptible than one containing 5% aluminium, 1½% iron, and 1½% manganese. However, brittle failures by intercrystalline fracture have been reported² in high-tensile β -brasses with aluminium contents as low as 0.78% and containing iron and manganese, suggesting that if the tests described by Bailey¹ had been carried on for more than 40 days further intercrystalline fractures might have occurred.

Bailey was unable to observe any structural feature which might account for the occurrence of intercrystalline cracking in these alloys, which, he could only suggest, must be inherently brittle.

Some indication of the possible nature of this "inherent" brittleness arises when account is taken: (i) of the nature of, and the differences between, the atomic arrangement within the grains and immediately in the vicinity of the grain boundaries in polycrystalline metals; and (ii) of the corresponding differences in mode of deformation under stress at the grain boundaries and in the interior of grains. It is generally considered that at grain boundaries the atomic arrangement is less regular than within the grains, the region being one of imperfect, so-called "transition" lattice structure. That motion between grains can occur at the grain boundaries in a viscous manner was first recognized by Rosenhain, who later,

with Archbutt, discussed the occurrence of intercrystalline failure in a wide range of metals as a result of relative movement between the crystals. Kê³ has more recently shown that grain boundaries do, in fact, behave in a truly viscous manner, that is, the shear-strain rate decreases rapidly with temperature. This is in contrast to the mode of deformation of the component crystals themselves, which is commonly by slip, a process requiring resolved shear stresses exceeding a critical value on particular crystal planes before it can occur and which, furthermore, is relatively insensitive to temperature.

It follows that, in a given material, intergranular flow at grain boundaries may, over certain ranges of temperature and strain rate, occur more readily than deformation of the grains themselves. Zener⁴ points out that the relaxation of shear stress at grain boundaries can lead to high stress concentrations within the grains, which may result in the formation of intergranular cracks, and Betteridge and Franklin⁵ have published micrographs indicating that such stress concentrations do in fact occur.

It may be expected of this type of failure that if intercrystalline fracture appears at a particular strain rate above a certain temperature, then if the strain rate is increased, the lowest temperature at which intercrystalline failure occurs will also be increased. It has to be recognized that there is at present no detailed understanding of the form of stress concentrations leading to fracture or of the intrinsic fracture strengths involved. While some information exists on the deformation characteristics of crystals under simple stress distributions in relation to composition, extent of prior deformation, and temperature, little or none is available on the flow properties of transition structures between the crystals in polycrystalline

* Manuscript received 15 October 1954. The work described in this paper was made available to members of The British Non-Ferrous Metals Research Association in confidential research reports issued in May 1949 and

February 1950.

† Formerly Investigator, The British Non-Ferrous Metals Research Association; now at Aluminium Laboratories, Ltd., Kingston, Ont., Canada.

material. The nature of the flow is not fully established, though both Kê³ and Mott⁶ have put forward hypotheses, that of Mott giving the correct magnitude of the effect without arbitrary parameters. Moreover, the composition of the transition structure is never altogether clear. In cast structures the intergranular regions are likely to contain concentrations of impurities either in solution or in precipitated form, but, apart from this, there is evidence from work on single-phase binary alloy systems⁷⁻¹¹ of so-called "equilibrium segregation" whereby, because the transition structure between grains is less regular than the structure within the grains, the concentrations of solute and solvent atoms in these regions, where equilibrium is established, may differ from the concentrations within the grains, to an extent depending on the misfit between adjacent grains, on the prior heat-treatment of the material, and on the solute content. Neither theoretical examination nor the available experimental evidence provide detailed information on the grain-boundary compositions concerned in relation to the factor just mentioned or on the modifying effects of solute elements additional to the first.

β -Brasses are notable in comparison with α -brasses for their high resistance to deformation at temperatures below, say, 500°C. This is presumably connected with the fact that they have an ordered structure at room temperature. On the other hand, there is no *a priori* reason to suppose that the properties of intergranular transition lattices in binary β -brasses differ greatly from those in binary α -brasses. The addition of aluminium as solute to β -brasses further increases the hardness of β -brass crystals, and may also affect the properties of the transition layers. It would be expected that an increase of hardness would permit the development of higher local stresses, and hence would increase the liability to failure by the type of mechanism considered.

In view of the foregoing discussion, it would not be surprising if binary β -brasses were subject to intergranular failure when loaded at ordinary temperatures, nor if the addition of aluminium within the single-phase range of contents influenced this liability. The purpose of the work to be described is first to show that the intergranular failures occurring in binary and ternary β -brasses are probably due to a mechanism of the kind proposed by Zener, and secondly to provide some evidence indicating that the effects of aluminium content may, at least in part, be exercised through modification of the grain-boundary structures.

Impact tensile tests at elevated temperatures and sustained tensile tests at room temperatures were carried out to investigate further the intercrystalline cracking of β -brasses, especially those containing aluminium. Metallographic and X-ray examination, supplemented by measurements of the electrode potentials of grain boundaries, were also carried out to see whether a correlation could be found between grain-boundary properties and the tendency to intercrystalline cracking.

II.—EXPERIMENTAL PROCEDURE

1. MATERIALS USED

The results given by Bailey¹ were obtained on alloys made from cathode copper, electrolytic (99.99%) zinc, and commercial-purity aluminium, and for convenience some of the compositions are included in Table I.

TABLE I.—Chemical Compositions of Alloys Investigated.

B.N.F. Mark	Cu, %	Zn, % (by diff.)	Al, %	Mn, %	Fe, %	Sn, %	Zr, %	Micro-structure As-Cast ‡	Average Grain-Dia., mm.
LXP *	56.25	38.32	2.05	1.28	2.10	$\beta + \text{Fe}^\dagger$	0.2
LXQ *	59.34	36.62	3.40	0.64	β	0.8
LXR *	62.98	32.91	4.11	β	0.1
MCE *	63.35	28.13	5.23	1.56	1.73	$\beta + \text{Fe}^\dagger$	0.3
MOF *	51.07	48.93	$\beta + \text{Fe}^\dagger$	2.8
NGP	63.57	32.14	4.29	β	0.6
NGO	59.84	35.87	4.29	$\beta + \gamma$	0.7
NHH	52.2	46.84	0.96	β	0.6
NCO	64.0	30.40	5.60	$\beta + \text{small amount of } \gamma$	0.6
NSN	51.0	49.00	β	3.9
NSF	57.9	38.75	3.35	$\beta + \text{small amount of } \gamma$	0.8
NSG	60.1	36.71	3.19	β	0.8
NSH	61.7	35.39	2.91	β	0.8
NSJ	63.1	33.77	3.13	$\beta + \text{small amount of } \alpha$	0.5
NYG	59.0	38.77	2.23	β	0.6
NYH	84.9	9.6	5.50	α	3.1
HPM †	63.70	32.30	4.00	β	0.4
HPH †	53.10	46.90	β	0.4

* Mechanical and stress-corrosion test results by Bailey.¹

† Extruded.

‡ Fe = Iron-rich constituent.

Other alloys examined were made from the same material, except that super-purity (99.99%) aluminium was used, thus reducing the iron content from 0.1–0.2% to less than 0.005%—the limit of detection by spectrographic methods. Spectrographic analysis also failed to show the presence of any impurities in these alloys, except traces of lead (<0.01%). Keel bars were cast in green sand moulds, and the material examined was taken from parts remote from the feeding head. The compositions of the alloys used are given in Table I.

2. TESTS UNDER SUSTAINED TENSILE STRESS

Loads were applied to 0.357-in.-dia. specimens by means of a calibrated spring acting through the end of a lever of ratio 11:1. Before testing, the machined specimens were pickled in 50% nitric acid, washed, and dried.

3. IMPACT TENSILE TESTS

A steel plate, split in the centre, was so cut that a specimen with rectangular ends and $\frac{3}{8}$ -in.-dia. gauge length could sit in the centre of the plate. A piece of asbestos sheet was secured to the bed of the Izod impact machine, and one-half of the steel plate was fixed to the asbestos sheet, the other half being placed on the asbestos sheet and aligned with the fixed half. The movable part of the plate had one

lug on each side, so that the falling hammer hit these lugs, subjecting the specimen to a rapid tensile strain. For tests at elevated temperature, the specimens were heated for 30 min. in a small furnace alongside the impact machine, one person taking the specimen out of the furnace and placing it in the steel plate while another released the hammer. By this procedure the time between taking the specimen out of the furnace and stressing was very short, so that the specimen temperature only fell by a very small amount. A full description of the apparatus has been given by Leech *et al.*¹²

4. METALLOGRAPHIC EXAMINATION

Unless otherwise stated, all specimens were electrolytically polished in 67% orthophosphoric acid, using a copper cathode. The voltage across the polishing cell was 1.8–2.0 V., and the current density was approximately 0.03 amp./cm.². Before electrolytic polishing, the specimen was taken down to 0000 emery, then polished with a metal polish such as "Bluebell", and degreased with acetone. To ensure that any flowed layer was completely removed, electrolytic polishing was continued for 40 min. For etching, the specimen was left in the polishing solution and the voltage reduced to 0.8 V. for approximately 1 min., though this time depended upon the material being etched, longer times being necessary for the β -brasses without aluminium than for those with it.

III.—RESULTS

1. METALLOGRAPHIC EXAMINATION

After electropolishing the material used in the tests described by Bailey,¹ pitting at the grain boundaries was observed in the brasses containing 3, 4, and 5% aluminium, whereas none was apparent in the brasses containing less than 3% aluminium.

(a) As-Cast Structures

The brasses used by Bailey¹ had been made from commercial-purity aluminium, and to be quite sure that the pitting was not caused by impurities introduced with the aluminium, a 4% aluminium brass was now made, using super-purity aluminium. Again grain-boundary pitting was observed, as it was in the 3% aluminium brasses NSG, NSH, and NSJ, which were also made from super-purity materials. Fig. 4 (Plate LIV) shows clean grain boundaries typical of alloys with less than 3% aluminium, while Figs. 6 and 7 (Plate LIV) show the grain-boundary pitting in brasses made from super-purity materials and containing 3 and 4% aluminium, respectively. In a 5% aluminium brass (NCC), some grain boundaries contained small γ particles, some showed coarse pits, and others showed fine pits (Fig. 7, Plate LIV) similar to those observed in the 3 and 4% aluminium brasses. The grain-boundary pitting appeared to become more severe as the aluminium content increased from 3 to 5%, but it by no means formed a

complete intergranular network, being generally found in one grain boundary but not in adjacent ones (see Fig. 5, Plate LIV). Whenever a grain boundary changed direction abruptly, a pit was generally observed (see Fig. 6, Plate LIV). It thus appears that grain-boundary pitting is a function of aluminium content only and not of purity.

(b) Insoluble Phase

The pitting might possibly be due to an insoluble phase being attacked during electropolishing. If this were so, then if the material was recrystallized, the pitting should remain in the same place, i.e. it would not be present at the new grain boundaries. The 4% aluminium β -brass (NGP) was cold worked and then annealed at 800° C., for 1 hr. After electropolishing, the pitting occurred at the new grain boundaries, and there appeared to be rather more of it. This proves indirectly that the pitting is not associated with an insoluble phase. Pitting was found at the grain boundaries of the annealed, extruded 4% aluminium β -brass HPM, a fact which also supports this view.

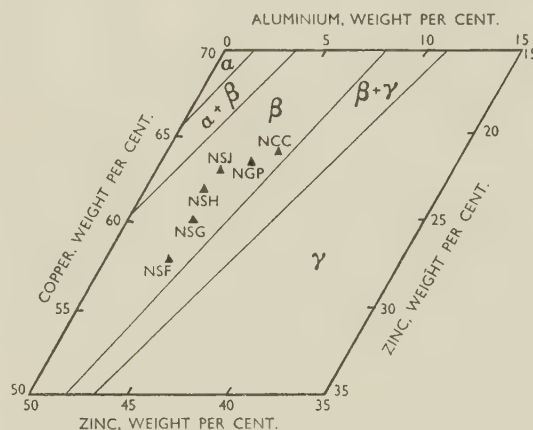


FIG. 1.—Solubility Limits at 800° C. (Bauer and Hansen.²¹)

(c) Soluble Phase

The possibility still remained that the pitting might be due to a phase which was soluble at high temperatures (e.g. small γ particles). To test this, specimens of the 3, 4, and 5% aluminium brasses (NSF, NSG, NSH, NSJ, NGP, and NCC) were heated at 800° C. for 1 hr., in oxygen-free nitrogen and quenched in water at room temperature. After this treatment all the 3% aluminium brasses had completely β structures but grain-boundary pitting was still present. This indicates that the pitting is not associated with any phase in the alloy system, for at 800° C. these alloys are in the middle of the β -phase field (see Fig. 1). After heat-treatment at 800° C., there was no change in the 4% aluminium brass, pitting still being present (see Fig. 8, Plate LIV), but there was a marked change in the case of the 5% aluminium brass. The massive γ and coarse pitting shown in Fig. 7 (Plate LIV) disappeared, and only the fine pitting remained. Reference will be made later to the coarse pitting. It is

therefore clear that the fine pitting is not due to a phase which can be taken into solution at 800° C., and the indications are that it is due to something other than a separate phase. Annealing the 4% aluminium brass for long periods at 400° C., caused no change in the structure, the pitting still occurring to the same extent. If the pitting was due to a separate phase such heat-treatment would probably have caused coagulation and hence larger pits. Confirmation was obtained by experiments on a 4% aluminium ($\beta + \gamma$) brass (NGO). On electropolishing the as-cast material, massive γ was observed within the grains and at the boundaries, but there was no grain-boundary pitting. After heating at 800° C. for 1 hr. and quenching, all the massive γ went into solution, and fine pitting was observed at some of the grain boundaries.

(d) Introduction of Aluminium by Diffusion

To examine further the effect of aluminium content on the occurrence of the fine pitting at the grain boundaries, specimens of 1 and 4% aluminium brasses (NHH and NGP) were immersed in molten superpurity aluminium (99.99%) for a short time so that a coherent coating was obtained. The specimens were then annealed at 600° C. for 3 and 2 days, respectively. On electropolishing, pitting was seen at a few of the grain boundaries near the aluminium coating in the 1% aluminium brass (see Fig. 9, Plate LIV). In the 4% aluminium brass small γ particles could be seen at a few of the grain boundaries near the coating (see Fig. 10, Plate LV), and on following these boundaries inwards, pits could be seen (Fig. 11, Plate LV). This indicates that there is preferential diffusion of aluminium along the grain boundaries, and also that the pitting represents a stage preceding the precipitation of the γ phase.

The above experiments show that the grain-boundary pitting is dependent upon the presence of aluminium, and the occurrence of the same effect in an aluminium α -brass was therefore considered possible. Examination of an as-cast 5% aluminium α -brass (NYH) showed that grain-boundary pitting was present, and when this material was cold worked and annealed, grain-boundary pitting was again observed at the new grain boundaries (Fig. 12, Plate LV). No pitting was observed at twin boundaries which, together with the fact that pitting was observed at the grain boundary between a twin and an adjacent grain but not at the grain boundary between the adjacent twin and the same grain (see Fig. 12, Plate LV), strongly suggests that the observed pitting depends upon the relative orientation of the neighbouring grains.

(e) Electron-Microscope Work

In what has gone before, reference had been made to pitting in the grain boundaries, but in fact it was not possible, by direct observation under the microscope, to be certain whether the effect was due to pitting or to the presence of a precipitate whose

structure was not resolved. In the hope that its high resolving power might lead to a solution of the problem, the electron microscope was used to examine Formvar replicas of electrolytically polished material.

Fig. 13 (Plate LV) shows a photograph ($\times 10,000$) of the fine pitting in the 5% aluminium brass (NCC) (cf. Fig. 7, Plate LIV). In prints of electron micrographs of replicas prepared by the Formvar process, dark areas correspond to depressions below the general surface, while light areas are caused by elevated regions of the specimen. The fine pitting seen under the light microscope in the 5% aluminium brass thus still appears as pitting when examined by the electron microscope. Fig. 14 (Plate LV) shows another boundary in the 5% aluminium brass (NCC) ($\times 10,000$) in which coarse pitting has been observed using the light microscope after electropolishing (Fig. 7, Plate LIV). Instead of pits the electron micrograph clearly shows particles; the dark areas surrounding these are most probably moats. The coarse pitting shown in Fig. 7 (Plate LIV) thus appears to be a fine precipitate of the γ phase which has been attacked during electropolishing. This is supported by the fact that on quenching the 5% aluminium brass (NCC) from a high temperature the coarse pitting disappears. It is not possible to say from the electron-microscope pictures whether the fine pitting is due to the presence of an even finer γ precipitate or to pitting in solute-rich areas. The fact that the fine pitting remains after quenching from a high temperature strongly suggests the latter.

To summarize, the grain-boundary pitting observed after electropolishing is dependent on the aluminium content and on the relative orientation of adjacent grains. This pitting cannot be explained by the presence of insoluble impurities or of particles of the γ phase.

2. ELECTROCHEMICAL WORK

The grain-boundary pitting described in the previous section strongly suggests that the presence of aluminium is making the grain boundaries more chemically active. Therefore the electrode potential of the grains and grain boundaries of brasses containing 0, 1, 3, and 4% aluminium (MCF, NHH, LXQ, and NGP, respectively) were measured in 3% sodium chloride solution, using the method described by Dix.¹³ The specimens were mounted in Bakelite, polished down to 0000 emery and then with Bluebell metal polish, followed by etching to reveal the grain boundaries and to remove the flowed layer. In order to isolate the grains from the grain boundaries, either the boundaries or the grains were painted out with a chlorinated rubber paint which is resistant to sodium chloride solution. When painting out the grains to leave the grain boundaries, a zone approximately $\frac{1}{16}$ in. wide was left.

The potentials were measured against a *N* calomel half-cell. The grain boundaries of the brasses containing 3 and 4% aluminium were found to be cathodic to the grains. No significant difference was found

between the boundaries and grains in brasses containing 0 and 1% aluminium. The measurements were repeated, using different etching reagents, as it was thought that the film left after etching might affect the result. The etching reagents used were ammonium persulphate with a little ammonia, 50% nitric acid, and a polish attack. In all cases the results were independent of the etching reagent employed.

Some time was necessary before the potentials became steady, but when this point had been reached, the grain boundaries were cathodic to the grain bodies by 25–30 mV. for the 3 and 4% aluminium brasses.

Potential measurements were also made on specimens polished on emery paper, in which both grains and grain boundaries were exposed. With the brasses containing 1 and 4% aluminium, there was hardly any difference in the steady potential (–340 mV.) and both were cathodic to the plain β -brass (steady potential –400 mV.). Comparing the 0 and 1% aluminium β -brasses, there was little difference in the copper and zinc contents, but a large difference in potential, whereas in the 1 and 4% aluminium brasses, there were large differences in the copper and zinc contents, but little differences in the potentials. The cathodic nature of the aluminium brasses in sodium chloride solution appears to be due to a change in the properties of the surface film caused by the presence of aluminium, rather than to changes in the copper:zinc ratio. Similarly, the cathodic nature of the grain boundaries observed by the Dix method was probably due to a high concentration of aluminium at the grain boundaries and consequent incorporation of alumina in the surface film. Although the potentials of the emery-polished surfaces showed no change as the aluminium content was increased from 1 to 4%, in the Dix method the most cathodic grain boundaries were observed in the 4% aluminium brass.

Since electropolishing in 67% orthophosphoric acid produced grain-boundary pitting in the 4% aluminium brass under these conditions, the grain boundaries were presumably anodic to the grain bodies. This was confirmed by the Dix method, the grain boundaries being 20–30 mV. more anodic than the grains. Moreover, the potential in 67% orthophosphoric acid of super-pure aluminium was –1.02 V., whereas that of plain β -brass was –0.33 V. If the grain boundaries were aluminium-rich, they would be expected to be preferentially attacked in this solution.

3. TESTS UNDER SUSTAINED TENSILE STRESS IN AIR

The β -brasses containing 3% or more of aluminium which failed with an intercrystalline fracture when stressed at the 0.1% proof stress in the work described by Bailey,¹ were very close to the $(\beta + \gamma)$ phase field. There was the possibility that the brittleness they exhibited was due to particles of the γ phase, since it is known that a β -brass with γ particles distributed at the grain boundaries will fracture in an intercrystalline manner.

To investigate this, a series of alloys containing 3% aluminium extending from the $(\beta + \alpha)$ to the $(\beta + \gamma)$ field was tested in air in the as-cast condition and after annealing at 800° C. for 1 hr. in oxygen-free nitrogen, followed by water-quenching. This heat-treatment made the brasses NSF and NSJ, which in the as-cast condition contained a very small amount of the γ and α phases, respectively, completely β . The position of the alloys in the β phase field is shown in Fig. 1. The mechanical properties are given in Table II, and the results of sustained tensile stress tests in Table III.

TABLE II.—Mechanical Properties of As-Cast Materials.

B.N.F. Mark	0.01% Proof Stress, tons/in. ²	0.1% Proof Stress, tons/in. ²	Elongation on $\sqrt{\text{Area}}$, %	Reduction of Area, %	U.T.S., tons/in. ²	Micro-structure
NSF	9.3	12.5	16	20	33.9	$\beta + \gamma$
NSG	11.2	15.7	14½	22	35.0	β
NSH	12.1	16.8	12	17½	32.6	β
NSJ	14.1	20.6	10	15	34.1	$\beta + \alpha$
NYG	9.3	13.8	17	22	31.0	β

TABLE III.—Results of Sustained Stress Tests in Air on β -Brasses Containing 3% Aluminium.

B.N.F. Mark	Condition	Cu, %	Zn, %	Al, %	Initial Stress, tons/in. ²	Failure Time
NSF 1	As-cast	57.9	38.75	3.35	25	1 hr.
NSF 2	As-cast and solution-treated	57.9	38.75	3.35	20	1 hr.
NSG 1	As-cast	60.1	36.71	3.19	20	5 days
NSG 2	As-cast and solution-treated	60.1	36.71	3.19	20	10 days
NSH 1	As-cast	61.7	35.39	2.91	20	>18 days*
NSJ 1	As-cast and solution-treated	63.1	33.77	3.13	25 20	3 days 20 days
NYG 1	As-cast	59.0	38.77	2.23	15	10 days

* Not failed in 18 days. Stress increased to 25 tons/in.².

The fractures of all the mechanical test specimens were transcrystalline, whereas those of all the specimens which failed under sustained tensile stress were intercrystalline. This observation immediately suggests that the rate of straining is an important factor in determining whether intercrystalline fracture occurs at room temperature. It is apparent from Table III that the failure time is shorter as the $\beta/(\beta + \gamma)$ boundary is approached; this may not be significant, however, as the 0.1% proof stress decreased, and the testing stress was therefore an increasing percentage of it, as the zinc content increased. It is interesting to note that the alloy NYG, containing 2% aluminium, failed, though an alloy containing 2% aluminium, 2% iron, and 1% manganese (LXP, Table I) did not fail in 40 days when stressed at twice its proof stress.¹ This agrees with Bailey's earlier observation that iron and manganese decrease the susceptibility to intercrystalline fracture. The fact that, after quenching from 800° C., all the above alloys were well within the β field shows that the observed intercrystalline fracture is not due to the presence of the γ phase.

4. LONGITUDINAL IMPACT TESTS AT LOW AND ELEVATED TEMPERATURES

As shown above, the tendency to intercrystalline fracture increases as the strain rate is reduced. If the rate of straining is increased intercrystalline fracture should occur when the temperature is raised.

Longitudinal impact tensile tests were carried out on plain β -brasses HPH (extruded and annealed 1 hr. at 300° C.), and NSN, and β -brasses containing 1–3% aluminium (NHH, NYG, NSG). Phosphorus-deoxidized copper was included for comparison. The results for copper are shown in Fig. 2, and Fig. 3 shows results for the 3% aluminium β -brass NSG. Fig. 3 is typical of the other brasses tested, the full results of which are given in Table IV.

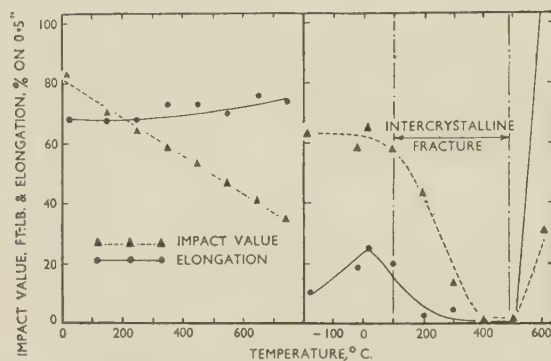


FIG. 2.

FIG. 3.

FIG. 2.—Longitudinal Impact Tensile Tests on Phosphorus-Deoxidized Copper.

FIG. 3.—Longitudinal Impact Tensile Tests on As-Cast 3% Al β -Brass (NSG).

TABLE IV.—Impact Tensile Results.

B.N.F. Mark	Condition	Cu, %	Zn, % (by diff.)	Al, %	Average Grain-Dia., mm.	Temp. Range (°C.) for Intercryst. Fracture
HPH	Extruded and annealed	53.10	46.90	...	0.4	100–400
NSN	As-cast	51.0	49.0	...	3.9	100–400
NHH	"	52.20	46.84	0.96	0.6	100–500
NYG	"	59.00	38.77	2.23	0.6	100–500
NSG	"	60.10	36.71	3.19	0.8	100–500

In contrast to the phosphorus-deoxidized copper, the β -brasses, both with and without aluminium, showed a decrease in elongation with increasing temperature, the elongation recovering at 400°–500° C. and 500°–600° C. for the alloys without and with aluminium, respectively. This very rapid increase in ductility at the higher temperatures is probably because the alloys became disordered. Both types of alloy started to give intercrystalline fractures at approximately 100° C., though the elongation of the aluminium-containing alloys decreased more rapidly than that of the aluminium-free. Grain-size seemed to have no effect on the temperature range for intercrystalline fracture, although the smaller grain-size material gave higher elongation and impact values than that

with coarse grain. Similar tests were also carried out on a 5% aluminium α -brass NYH. In this case, although the elongation decreased with increasing temperature, no intercrystalline failure was obtained.

5. EXAMINATION OF INTERCRYSTALLINE FRACTURES

As the grain-size of the materials used in this work was larger than a normal X-ray beam, it was possible after fracture to examine the intercrystalline facets by means of X-rays. Accordingly, back-reflection Laue photographs, using unfiltered cobalt radiation, were taken from facets in the intercrystalline fracture. The specimens were mounted in Plasticine with the facet under examination normal to the X-ray beam of dia. 1 mm. Photographs were also taken from the same intercrystalline facets after successive electropolishing operations to see how the structure changed with distance from the grain-boundary surface. During electropolishing, the specimen was protected by paraffin wax except for the facet under examination, and the number of coulombs passed during polishing was measured. The area of the facet was determined by projecting it on to a screen of a Vickers projection microscope, and from the electrochemical equivalent previously determined and the density, the thickness removed during polishing was calculated. As the intercrystalline facets were not perfectly flat, more metal would be removed from the elevated regions of the facets during electropolishing, and so the calculated figures should only be regarded as approximate.

(a) Examination of Intercrystalline Fractures Produced by Sustained Tensile Stressing

Facets at approximately 45° to the direction of stress, in a fractured specimen of a 3% aluminium β -brass (NSG), were examined. Figs. 16 and 17 (Plate LVI) show the Laue patterns from one of the facets before and after pickling in 50% nitric acid for 10 min. The diffuseness of the spots in Fig. 16 shows that there is a heavily worked layer at the facet surface. After etching away a thin layer, the spots were sharp (Fig. 17), showing the grains to be almost completely strain-free.

(b) Examination of Intercrystalline Fractures Produced in the Longitudinal Impact Test

The specimens examined were those of a 3% aluminium β -brass (NSH) which had been fractured at 400° and 500° C. At these temperatures specimens broke with a completely intercrystalline fracture (see Fig. 15, Plate LV), and furthermore gave no measurable elongation. Facets approximately (i) normal, (ii) at 45°, and (iii) parallel, to the direction of stress were examined in triplicate.

(c) Effect of Orientation of Facet with Respect to Direction of Stress

(i) Facets Approximately Perpendicular to Stress.—In general, these facets gave a Laue pattern of sharp spots. Fig. 18 (Plate LVI) shows such a photograph

from a facet in a specimen which had been fractured at 500° C. In some cases, whilst the Laue pattern consisted of sharp spots, each had a diffuse tail, i.e. asterism (see Fig. 19, Plate LVI). This is interpreted as meaning that the facet had a thin, slightly deformed surface layer, the depth of which was much less than the penetration depth of the X-radiation. The depth at which the reflected intensity of the cobalt radiation is reduced to 10% of the incident intensity was calculated, using the mass-absorption coefficient of copper, to be about 16 μ . One facet gave a Laue pattern of diffuse spots, showing that there was a lightly deformed zone having a depth greater than the depth of penetration of the X-radiation.

(ii) *Facets at Approximately 45° to Stress.*—These facets gave strong arcs of Debye-Scherrer rings from the $K\alpha$ and/or $K\beta$ component in the radiation. Usually the Laue pattern was too diffuse to be seen, though occasionally very diffuse reflections from the prominent zones were apparent. Fig. 20 (Plate LVI) shows such a pattern obtained from a facet at approximately 60° to the direction of stress in a specimen which had been fractured at 400° C. It will be noticed that the $K\alpha_1$ and $K\alpha_2$ arcs are clearly resolved, which indicates that the crystallites formed by the deformation have probably recovered. This recovery may have taken place during the tests or in the 5 min. after fracture, which was the time taken for the specimens to cool down to room temperature. It is clear, however, that these facets have suffered more deformation during fracture than those perpendicular to the stress. After removing a thickness of approximately 16 μ from this same facet, a sharp Laue pattern with faint asterisms was obtained (see Fig. 21, Plate LVI). Removal of a further 6 μ gave completely sharp Laue spots. The deformed layer on this facet was therefore 16–22 μ deep.

(iii) *Facets Nearly Parallel to the Direction of Stress.*—For facets more nearly parallel to the direction of stress, the X-ray patterns, besides showing arcs of Debye-Scherrer rings, showed increasing numbers of sharp spots lying on rings through these arcs. Figs. 22 and 23 (Plate LVII) show patterns from facets in the same specimen as that used for Fig. 20 (Plate LVI), and which were at 30° and 0° to the direction of stress, respectively. Presumably the amount of deformation on these facets was so great that, at the testing temperature of 400° C., recrystallization had taken place.

On removal of 18 μ from the facet at 30° to the direction of stress, the X-ray pattern consisted of diffuse Debye-Scherrer arcs with a few faint, sharp spots on the Debye-Scherrer ring. Faint, diffuse Laue spots could also be seen. Removing a further 14 μ gave a pattern of diffuse Laue spots, though a trace of the Debye-Scherrer arc still remained. Thus, removal of 32 μ from this facet was sufficient to remove the heavily deformed layer, leaving a layer which was only lightly deformed. After removing a further 16 μ the Laue pattern was much stronger, though still

showing a diffuse asterism. The thickness of the deformed zone on this facet is thus not less than 48 μ and probably, bearing in mind the penetration depth of the X-radiation, not more than 64 μ .

After electropolishing the facet in the direction of stress, the X-ray pattern remained unchanged until approximately 100 μ had been removed; at this stage the ring of sharp spots disappeared, leaving a Debye-Scherrer arc (see Fig. 24, Plate LVII). Thus the depth of the layer giving rise to the sharp spots was much greater on this facet than on that at 30° to the direction of stress. The Debye-Scherrer arcs remained until an additional 100 μ had been removed, when the pattern consisted of diffuse Laue spots. The thickness of the deformed zone is therefore of the order of 200 μ .

From the foregoing it is concluded that the degree of deformation and the depth of the deformed layer at the surface of these intercrystalline facets increases as the angle between the facet and direction of stress decreases from 90° to 0°.

(d) *Microscopical Examination of Intercrystalline Fractures*

Sections of fractures taken from impact tensile specimens that had been tested at elevated temperatures were microscopically examined to see whether a thin recrystallized zone was present which would account for the sharp spots on the Debye-Scherrer rings in Figs. 22 and 23 (Plate LVII). It was not possible, however, to examine the same facets as were examined by X-rays, because their fractured surfaces were destroyed during electropolishing. Examination showed that small recrystallized grains were present at the surface of some facets, a typical example being shown in Fig. 25 (Plate LVII).

The tendency for these new recrystallized grains to occur was greater on facets more nearly parallel to the stress than on facets of other orientations. In some cases, however, facets parallel, or at a small angle, to the direction of stress showed no such zone of recrystallized grains, though it must be remembered that a microsection is only a plane through the facets and, had these sections been ground down more, recrystallized grains might have been observed. That this is probably correct is shown by the fact that, on repolishing a section of a fracture, the original recrystallized grains disappeared and others occurred at a different place along the section of the same facet. This observation strongly suggests that the deformed surface zone is not uniform over the facet surface. Support for this view was obtained during the X-ray examination. Besides the surface recrystallized grains, it was observed that there was a tendency for recrystallized grains to occur at the junction of two grains (see Fig. 26, Plate LVII), thus showing that, at these junctions, intense plastic deformation had taken place. Moreover, recrystallized grains could often be seen at the ends of intercrystalline cracks well removed from the fracture (see Fig. 27, Plate LVII).

From the above results it follows that, although the

specimens may break with no measurable elongation or reduction in area, there exists on the exposed grain-boundary surfaces in the intercrystalline fracture, a plastically deformed zone, the degree of deformation and depth of which increase as the grain-boundary surface more nearly approaches the direction of stress. At grain-boundary surfaces near or perpendicular to the direction of stress, there is little or no plastic deformation; hence it appears that at these surfaces the fracture is almost perfectly brittle.

IV.—DISCUSSION OF RESULTS

1. GRAIN-BOUNDARY CONCENTRATIONS

The presence of grain-boundary precipitate is generally postulated to account for intercrystalline brittleness and also for stress-corrosion. There are obvious difficulties in explaining the metallographic observations in terms of a second phase or of an insoluble impurity because (a) grain-boundary pitting was observed in alloys which were situated in the centre of the β phase field, (b) pitting occurred in alloys made from super-purity materials, (c) pitting was still present at grain boundaries after recrystallization, (d) no coalescence took place on long heating, (e) pitting still remained after quenching from a high temperature (800° C.), and (f) no precipitate was seen on the facets of intercrystalline fractures. In addition, the mode of fracture was a function of the rate of straining. This would not be so if the grain-boundary pitting were due to small particles of the γ phase. Whitaker¹⁴ showed that a ($\beta + \gamma$) brass, with the γ distributed at the grain boundaries, fails with an intercrystalline fracture irrespective of the rate of straining.

On the other hand, it is possible to explain the occurrence of fine pitting by "equilibrium segregation", according to which solute atoms that differ in size from the solvent spaces they fill tend to segregate to dislocated regions such as grain boundaries. In the equilibrium state there should accordingly be a segregation of large and/or small solute atoms at the grain boundary, the degree of segregation depending upon the relative orientation of the neighbouring grain and the solute concentration. Experimental evidence has been given by McLean and Northcott,^{7, 8, 15} Samuels⁹ for bismuth in copper, and Perryman^{10, 11} for iron in aluminium and tin in copper-tin alloys. The difficulties in obtaining direct evidence for these concentrations are considerable, and the experimental evidence given by these authors is of an indirect nature. The most direct evidence for this type of segregation has been given by Chalmers *et al.*,¹⁶ who showed, using radioactive tracers, that polonium, which is the decay product of Bi²¹⁰, segregated on the grain boundary in bismuth-lead alloys.

Support for the hypothesis that in these aluminium β -brasses the concentration of aluminium at the grain boundaries is greater than that within the grains is given by the fact that the grain boundaries were found

to be cathodic to the grains in sodium chloride solution but anodic to the grains in phosphoric acid.

Although the experimental evidence reported here indicates a segregation of aluminium at the grain boundaries, it is possible that there may also be segregation of zinc, for Cottrell¹⁷ has shown that binary β -brass single crystals exhibit a stepped stress/strain curve and has concluded that zinc segregates at the dislocations, making it reasonable to suppose that zinc may concentrate at the grain boundaries. However, since the aluminium atom is about 10% larger than the copper atom, whereas the zinc atom is only 7% larger, there may well be a greater tendency for aluminium to concentrate at the grain boundaries than for zinc to do so.

2. MECHANISM OF FRACTURE

It is now generally recognized that the grain boundary is a transition lattice between the two neighbouring grains, and there is a great deal of experimental evidence⁴ to show that grain boundaries can behave in a viscous way, as envisaged by Rosenhain. Kê has shown that the activation energy for grain-boundary flow is similar to that for self-diffusion, which, in general, is roughly proportional to the latent heat of fusion. Mott⁶ has also put forward a theory to account for Kê's results, which again gives the activation energy proportional to the latent heat of fusion. As the latent heat of fusion is approximately proportional to the melting point, it thus appears that, for a pure metal, the higher the melting point, the less is the grain-boundary flow under given conditions.

Kê³ has shown that grain-boundary flow under a small stress resulted in creep until the elastic stresses in the crystals were such as to relieve the boundaries of shear stresses. Deformation under a high stress will proceed in the same way, but localized plastic deformation of the crystals or local fracture may occur. The tendency to intercrystalline fracture will be a function of the viscous properties of the grain boundaries and also of their fracture characteristics.

It is clear that the tendency to intercrystalline fracture will be greater if the grains are very hard and the grain boundaries are in such a condition that viscous flow can take place easily. An analogous case would be a duplex alloy in which the phase at the grain boundaries was more ductile than the remainder of the grain.¹⁸ Thus, increasing the zinc and aluminium contents will make the grains harder, which will permit the development of higher local stresses and so increase the tendency to intercrystalline fracture; aluminium is a much more powerful hardening element than zinc, and so will be far more effective in this respect. The tendency to intercrystalline flow and fracture should therefore increase with increasing aluminium and zinc content. This contention is supported by the results on the β -brasses, and also by the fact that no intercrystalline fracture was obtained in the relatively ductile 5% aluminium α -brass NYH.

High concentrations of aluminium and/or zinc at the grain boundaries may also affect both the viscous flow and fracture process. The fact that the binary β -brasses failed with an intercrystalline fracture in the impact tensile test indicates that if Bailey¹ had carried his tests on for longer times, intercrystalline fracture might have been obtained in those brasses containing less than 3% aluminium.

Although the above description of the mechanism of intercrystalline fracture is supported in a general way by the results of the X-ray examination of fractured surfaces, it is felt that viscous slip by itself would be unlikely to produce such thick plastically deformed zones as were shown to exist on the surfaces of facets inclined to the direction of stress. Grain-boundary surfaces, however, have many irregularities which, even though they may be very small, will limit the movement of viscous flow. These limitations on the viscous flow will cause stress concentrations to be

built up at the irregularities and grain corners and localized plastic deformation will take place. Figs. 26 and 27 (Plate LVII) support this contention. Supporting evidence for the localized nature of the plastic deformation over the facet surface is obtained in the observation that on repolishing a section of a fracture, the original recrystallized grains disappeared and others occurred at a different place along the section of the same facet. The movement resulting from this localized plastic deformation will then cause a gross relative movement at the grain boundaries, such as that described by Hanson and Wheeler¹⁹ and King²⁰ *et al.*

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REFERENCES

1. A. R. Bailey, *Metal Ind.*, 1952, **80**, 519.
2. T. L. Sheehan and H. E. Dickerman, *J. Amer. Soc. Naval Eng.*, 1946, **58**, 586.
3. T'ing-Sui Kê, *Phys. Rev.*, 1947, [ii], **71**, 533; **72**, 41; 1948, [ii], **73**, 267.
4. C. M. Zener, "Elasticity and Anelasticity of Metals", p. 147. 1948: Chicago (University of Chicago Press).
5. W. Betteridge and A. W. Franklin, *J. Inst. Metals*, 1951-52, **80**, 147.
6. N. F. Mott, *Proc. Phys. Soc.*, 1948, **60**, 391.
7. D. McLean and L. Northcott, *J. Iron Steel Inst.*, 1948, **158**, 169.
8. D. McLean, *J. Inst. Metals*, 1947, **73**, 791 (discussion).
9. L. E. Samuels, *ibid.*, 1949-50, **76**, 91.
10. E. C. W. Perryman, *Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197**, 911.
11. E. C. W. Perryman, *ibid.*, 906.
12. E. A. Leech, P. Gregory, and R. Eborall, *J. Inst. Metals*, 1954-55, **83**, (7), 347.
13. E. H. Dix, Jr., *Trans. Amer. Inst. Min. Met. Eng.*, 1940, **137**, 11.
14. M. E. Whitaker, *Metallurgia*, 1948, **39**, 21, 66.
15. D. McLean and L. Northcott, *J. Inst. Metals*, 1946, **72**, 583.
16. M. T. Stewart, R. Thomas, K. Wauchope, W. C. Winegard, and B. Chalmers, *Phys. Rev.*, 1951, [ii], **83**, 657.
17. G. W. Ardley and A. H. Cottrell, *Proc. Roy. Soc.*, 1953, [A], **219**, 328.
18. E. C. W. Perryman and J. C. Blade, *J. Inst. Metals*, 1950, **77**, 263.
19. D. Hanson and M. A. Wheeler, *ibid.*, 1931, **45**, 229.
20. R. King, R. W. Cahn, and B. Chalmers, *Nature*, 1948, **161**, 682.
21. O. Bauer and M. Hansen, *Z. Metallkunde*, 1932, **24**, 1, 73, 104.

1607 THE EFFECT OF ZIRCONIUM AND TITANIUM ON THE INTERCRYSTALLINE-CRACKING TENDENCY OF BETA-BRASSES *

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(Communication from The British Non-Ferrous Metals Research Association.)

SYNOPSIS

Solute elements of unfavourable size-factor tend to form equilibrium segregates at grain boundaries. If the solute element is of high melting point, it is unlikely to diffuse readily in the solvent, and should accordingly increase the effective viscosity of the grain boundaries.

The addition to β -brasses of suitably chosen elements of high melting point might, on these simple grounds, be expected to increase the resistance of the grain boundaries to the relaxation of shear stress, and thereby decrease the liability of these materials to intergranular fracture.

Small additions of zirconium and titanium were made to β -brasses of three compositions. Impact and sustained tensile tests revealed improvement in the properties of two of them.

I.—INTRODUCTION

It has been shown by Bailey¹ that β -brasses containing 3% or more of aluminium fail with an intercrystalline fracture when stressed at about the 0.1% proof stress in air, or in some inert environment such as liquid paraffin. Stressing in 3% sodium chloride solution was found to increase slightly the rate of cracking. Later work by Perryman² showed that aluminium probably promotes this type of failure, because of (i) its marked hardening effect, and (ii) the concentration of aluminium and/or zinc at the grain boundaries. Both of these factors would make grain-boundary slip more likely to occur.

As a result of Eborall's work³ on the effect of additions on the hot-working properties of tin bronzes, preliminary experiments⁴ were carried out to see if similar additions, selected on the bases of (i) an "unfavourable" size-factor (i.e. an atomic diameter differing appreciably from that of the solute), and (ii) a high melting point, lessened the tendency to intercrystalline flow and fracture of β -brasses. A marked improvement was obtained, and the work to be reported here is a continuation of this preliminary investigation.

Small additions of zirconium and titanium were made to (1) β -brasses containing nominally copper 52, zinc 48, and aluminium about 0.1%, (2) β -brasses containing copper 63, zinc 33, and aluminium 4%, and (3) complex β -brasses (to B.S. 1400-HTB3-C) containing copper 63, zinc 29, aluminium 5, iron 1.5,

and manganese 1.5%. Impact-tensile tests and tests under sustained tensile stress in 3% sodium chloride solution were carried out to evaluate the effect of these additions on the tendency to intercrystalline flow and fracture. Alloys with and without additions, in all three groups, were tested in the as-cast condition, and tests were also carried out on the 4% aluminium β -brasses in the wrought condition.

II.—EXPERIMENTAL PROCEDURE

High-purity materials were used and, to facilitate making additions to the binary β -brasses, 0.1% aluminium was added as a deoxidant. The zirconium was added as copper-zirconium hardener alloy made either by melting and casting a copper-10% zirconium pressed-powder compact in vacuum or by melting a pressed-powder compact in a reducing atmosphere. This method gave clean castings. The titanium was added as copper-30% titanium alloy.

The chemical compositions of the alloys examined are given in Table I, with the results of spectrographic examination for impurities. Significant amounts of impurity were found only in the complex brasses OFN 47 and OHW 13, 0.02% lead and 0.001% bismuth being found in OFN 47 and 0.06% lead and 0.001% bismuth in OHW 13.

Keel bars were cast in green-sand moulds and all test-pieces were taken from parts remote from the feeding head. Aluminium β -brasses to be tested in

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TABLE I.—Analyses of Alloys Investigated.

Alloy Type	B.N.F. Mark	Cu, %	Zn, % (by diff.)	Al, %	Other Addn., %	Impurities, by Spectrographic Analysis, % *
β -Brass (sand-cast)	OFN 15	51.8	48.1	0.09	...	<0.01 Pb
	OFN 11	52.1	47.7	0.10	0.05 Zr	<0.01 Fe, <0.01 Pb, 0.01 Mn
	OHW 1	51.8	48.2	0.01	0.01 Ti	<0.01 Fe
Aluminium β -Brass (sand-cast)	OFN 3	63.6	32.4	3.93	...	<0.01 Fe, <0.01 Pb, <0.01 Sn
	OFN 16	62.6	33.3	4.03	0.05 Zr	<0.01 Fe, <0.02 Si
	OFN 26	61.1	34.8	3.79	0.21 Zr	0.03 Fe, ~0.05 Si, <0.01 Sn
	OFN 29	62.3	33.2	4.05	0.35 Zr	~0.05 Fe, ~0.05 Sn
	OHW 4	62.5	33.5	3.92	0.05 Ti	...
Complex β -Brass (sand-cast)	OFN 44	60.6	31.7	4.63	1.95 Fe 1.07 Mn	<0.02 Si, 0.01 Ni
	OFN 48	61.7	31.4	4.12	2.02 Fe 0.72 Mn	<0.02 Si, 0.01 Ni
	OFN 47	61.0	32.0	4.25	1.92 Fe 0.78 Mn 0.03 Zr	<0.02 Si, 0.02 Pb 0.01 Ni, 0.001 Bi
	OHW 13	61.4	31.6	4.02	1.96 Fe 0.84 Mn 0.08 Ti	0.06 Pb, <0.02 Si 0.01 Ni, 0.001 Bi
Aluminium β -Brass (chill-cast and hot rolled)	OFN 30	62.9	33.1	3.96	...	<0.01 Fe, ~0.001 Bi
	OFN 38	62.7	33.4	3.94
	OFN 39	62.6	33.3	4.00	0.055 Zr	...
	OHW 11	63.0	32.9	4.03	0.065 Ti	...

* Limits of detection by spectrographic analysis: Ni, 0.01; Pb, 0.005; Sn, 0.005; Si, 0.01; Bi, 0.001; Sb, 0.001; Mn, 0.01; Fe, 0.005; As, 0.002; P, 0.01; Ti, 0.01; Zr, 0.01%.

the wrought condition were chill-cast in cast-iron moulds by a semi-Durville process, scalped, cut into bars, $1\frac{1}{4} \times 1\frac{1}{4} \times 8$ in., and hot-rolled to rod according to the schedule given in Table II.

TABLE II.—Hot Working of 4% Aluminium β -Brasses.

B.N.F. Mark	Addn. Elements, %	Soaking Temp. Before Rolling, °C.	Intermediate Annealing Temp., °C.	No. of Intermediate Anneals	Temp. of Last Anneal, °C.	Reduction in Area (%) After Last Anneal	Total Reduction in Area, %
OFN 30	...	650	650	1	650	35	75
OFN 38	...	700	700	5	650	33	83
OFN 39	0.055 Zr	650	650	14	650	12	83
OHW 11	0.065 Ti	650	650	7	650	25	83

Impact tensile tests were carried out by the method described in a previous paper.² Sustained tensile tests in 3% sodium chloride solution were carried out, using specimens of 0.357 in. dia. to which loads were applied by a calibrated spring acting on a lever of ratio 11:1. The specimen was partially immersed in a 3% sodium chloride solution which was topped up daily and renewed every 4 weeks.

III.—RESULTS

1. MICROSCOPICAL EXAMINATION

All the brasses were essentially of the β phase, no α or γ phase being detected. The complex brasses containing iron and manganese showed particles of an iron-rich phase, and those to which additions of zirconium or titanium had been made showed small particles of some other phase associated with these addition elements.

With increasing zirconium content in the sand-cast alloys, the second phase, which appeared mainly at the grain boundaries, increased in amount: with 0.35% zirconium present (alloy OFN 29) nearly every boundary contained films of the second phase, as shown in Fig. 1 (Plate LVIII). Some of these second-phase particles could be taken into solution by soaking at 800° C. A similar structure was observed in the chill casting (OFN 39) from which the wrought material was prepared (Fig. 2, Plate LVIII) and in the titanium-bearing alloys, as, for example, in Fig. 3 (Plate LVIII) (OHW 11). Hot rolling the chill-cast materials broke up the intergranular films of the zirconium- or titanium-rich phase into strings of

TABLE III.—Mechanical Properties of Cast and Wrought β -Brasses.

B.N.F. Mark	Nominal Compn., %	Addn., %	U.T.S., tons/in. ²	0.01% Proof Stress, tons/in. ²	Reduction in Area, %	Elongation, %	Young's Modulus, lb./in. ² $\times 10^6$	Average Grain Dia., mm.
OFN 15	52 Cu, 48 Zn, 0.1 Al	...	26.8	4.4	35½	37	12.7	2.5
OFN 11	" " "	0.05 Zr	28.9	3.6	29	37	10.7	3.8
OHW 1	" " "	0.01 Ti	27.3	3.7	32	36	13.3	2.6
OFN 3	63 Cu, 33 Zn, 4 Al	...	38.0	22.4	10	12	13.1	1.5
OFN 16	" " "	0.05 Zr	41.2	22.4	15	18	14.4	1.2
OHW 4	" " "	0.05 Ti	41.2	22.0	15	18½	14.0	1.0
OFN 48	61 Cu, 32 Zn, 2 Fe, 0.8 Mn, 4 Al	...	45.1	24.8	15½	13	15.4	0.3
OFN 47	" " " "	0.03 Zr	46.0	24.0	21	19	15.6	0.3
OHW 13	" " " "	0.08 Ti	46.3	25.1	20	18½	14.9	0.2
OFN 30 *	63 Cu, 33 Zn, 4 Al	...	35.2	22.0	14	10	12.1	1.4
OFN 38 †	" " "	...	36.4	20.5	14½	12½	12.7	1.3
OFN 39 ‡	" " "	0.06 Zr	38.3	18.9	22	21	10.8	1.4
OHW 11 ‡	" " "	0.06 Ti	39.0	20.8	20	17	12.0	1.3

* Hot-rolled and soaked at 800° C. for 1 hr. and quenched in cold water.

† Hot-rolled and soaked at 650° C. for 1 hr. and quenched in cold water.

‡ Hot-rolled and soaked at 800° C. for 1 hr., then furnace-cooled to 650° C. and quenched in cold water.

particles; after final recrystallization at 800° C., this phase was still present at positions corresponding to the original grain boundaries.

Examination of a 5% aluminium β -brass containing 0.2% zirconium (not referred to in Table I) showed the presence of the copper-zirconium eutectic. During etching in a 20% solution of hydrofluoric acid containing 1% nitric acid,³ an unidentified phase was attacked (Fig. 4, Plate LVIII) (OFN 26). Similar observations were made when the copper-zirconium hardeners were examined. The copper-zirconium eutectic was not observed in any of the 4% aluminium β -brasses containing up to 0.35% zirconium, but after etching in the acid mixture, the small second-phase particles were attacked. It appears that these small particles are not associated with the copper-zirconium system, but may be intermetallic compounds of zirconium with some impurity.

Examination after electropolishing and electrolytic etching, using the methods described in a previous paper,² revealed fine grain-boundary pitting in both as-cast and heat-treated zirconium-bearing brass OFN 11 (see Fig. 5, Plate LVIII). No such pitting could be seen in the titanium-bearing brass OHW 1, nor in the plain copper-zinc alloy OFN 15, both of which showed clean grain boundaries. During electropolishing, the second phase associated with the zirconium addition was attacked, and it is possible that the fine grain-boundary pits were due to attack of very small particles of this phase. Examination of the same specimen after mechanical polishing and etching revealed small amounts of the second phase within the grains, but no fine dispersion of this phase could be seen at the grain boundaries. The fine pitting may be due to attack at zirconium-rich grain boundaries similar to that observed in the ternary aluminium β -brasses.² Additional indication that zirconium concentrates at the grain boundaries was obtained after examining the zirconium-bearing 4% aluminium brass OFN 16. In this case the grain-

boundary pitting was much more abundant than in the 4% aluminium brass OFN 3. No metallographic features were observed to suggest that titanium concentrates at the grain boundaries.

2. MECHANICAL TEST RESULTS

The results of tensile tests are given in Table III, each result being the mean of two tests. In general the titanium and zirconium additions had no great effect on the tensile properties. There was no significant effect on the properties of the 0.1% aluminium β -brass. The additions increased slightly the U.T.S. and the ductility of the ternary 4% aluminium β -brass and the complex alloy OFN 48. The increase in ductility was much more apparent for the wrought than for the cast alloys. In no case did the additions cause any significant change in the 0.1% proof stress.

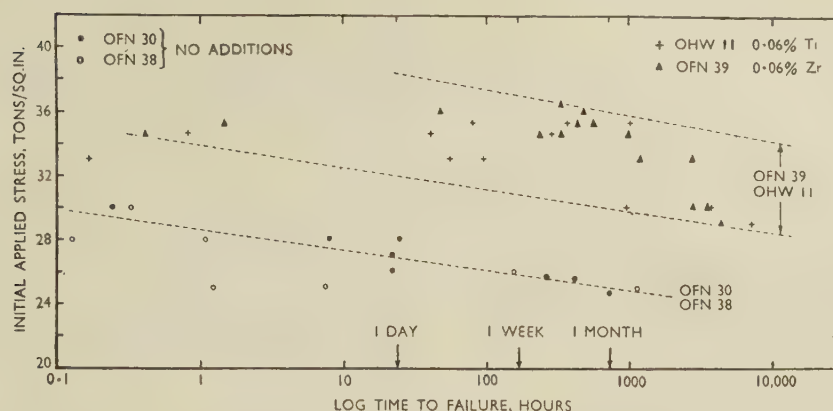
3. IMPACT TENSILE TESTS

The main effect of the addition elements was to decrease the temperature range in which intercrystalline fracture took place. The results are summarized

TABLE IV.—Results of Impact Tensile Tests.

B.N.F. Mark	Condition	Cu, %	Zn, %	Al, %	Addn., %	Temp. Range for Intercrystalline Fracture, °C.
OFN 15	As cast	52	48	0.1	...	100-400
OFN 11	"	52	48	0.1	0.05 Zr	Intercryst. fracture at 400° C. only
OHW 1	"	52	48	0.1	0.01 Ti	300-400
OFN 3	"	63	33	4	...	100-500
OFN 16	"	63	33	4	0.05 Zr	300-500
OHW 4	"	63	33	4	0.05 Ti	200-500
OFN 38	Wrought and heat-treated	63	33	4	...	100-500
OFN 39	" "	63	33	4	0.055 Zr	400-500
OHW 11	" "	63	33	4	0.065 Ti	200-500

in Table IV. The temperature ranges are approximate because specimens were tested only at 100° C. intervals.

FIG. 6.—Effect of Titanium and Zirconium on Stress-Corrosion of Wrought 4% Aluminium β -Brass.

It is apparent from Table IV that zirconium is a more effective addition than titanium. The additions had little effect on the energy to fracture or elongation.

4. SUSTAINED TENSILE TESTS IN 3% SODIUM CHLORIDE SOLUTION

Preliminary sustained tensile tests on a 3% aluminium β -brass showed that the addition of 0.04% zirconium increased the resistance to fracture whether the test was carried out in 3% sodium chloride solution or in air. Further tests were carried out on some of the materials shown in Table I. Table V gives the

TABLE V.—Effect of Zirconium and Titanium on the Life under Sustained Tensile Stress of Cast 4% Aluminium β -Brass Specimens Partially Immersed in 3% Sodium Chloride.

B.N.F. Mark	Ordinary Mechanical Properties				Initial Applied Stress, tons/in. ²	Life, days
	U.T.S., tons/in. ²	0.1% Proof Stress, tons/in. ²	Elongation, %	Reduction in Area, %		
OFN 3 (no addn.)	38.0	22.4	12	10	20 25 25 30 30	Unbroken after 183 days 4 10 1 2
OFN 16 (0.05% Zr)	41.2	22.4	18	15	25 30 30	35 8 11
OHW 4 (0.05% Ti)	41.2	22.0	18½	15	25 25 30 30	22 37 1 2

results of tests on as-cast 4% aluminium β -brasses both with and without additions. Both 0.05% titanium and 0.05% zirconium increased the time to fracture, zirconium appearing to be more effective than titanium.

Table VI gives the results of tests on the wrought 4% aluminium β -brasses, and the results are plotted in Fig. 6. Although there is considerable scatter it is apparent that the titanium and zirconium additions have effected a considerable improvement in the

resistance to delayed fracture, zirconium usually being the more effective. For example, brasses containing titanium or zirconium lasted 200–300 days when stressed at 29 tons/in.², whereas the life of the plain alloy was only a few minutes at this stress (the mechanical properties were similar except that the

TABLE VI.—Effect of Zirconium and Titanium Additions on the Life under Sustained Tensile Stress of Wrought 4% Aluminium β -Brass Specimens Partially Immersed in 3% Sodium Chloride.

B.N.F. Mark	Ordinary Mechanical Properties				Average Grain Dia., mm.	Initial Applied Stress, tons/in. ²	Life, days (unless otherwise stated)
	U.T.S., tons/in. ²	0.1% Proof Stress, tons/in. ²	Elongation, %	Reduction in Area, %			
OFN 30 (no addn.)	35.2	22.0	10	14	1.4	24.6 25.5 25.6 26 27 28 28 30	30 17 11 1 1 1 8 hr. 15 min.
OFN 38 (no addn.)	36.4	20.5	12½	14½	1.3	25 25 26 28 28 30 33	48 7½ hr. 1½ hr. 6½ 8 min. 65 min. 20 min. 3 min.
OFN 39 (0.06% Zr)	38.3	18.9	21	22	1.4	29 30 30 33 33 34.6 34.6 34.6 35.3 35.3 35.3 36 36 36.5	184 116 149 116 50 41 14 25 min. 10 22 18 1½ hr. 20 2 14
OHW 11 (0.06% Ti)	39.0	20.8	17	20	1.3	29 30 30 33 33 34.6 34.6 34.6 35.3 35.3 35.3 35.3	297 158 40 4 2½ 10 min. 41 hr. 50 min. 12 15½ 3½ 43

U.T.S. of the plain alloy was 2-3 tons/in.² lower than the others).

The improvements effected by the zirconium and titanium additions in these tests are in the same direction as, and are more impressive than, the results of the impact tensile tests.

Table VII gives the results of sustained tensile tests on as-cast 4% aluminium β -brasses containing iron

TABLE VII.—*Effect of Zirconium and Titanium on the Life under Sustained Tensile Stress of Cast Complex β -Brass Specimens Partially Immersed in 3% Sodium Chloride.*

B.N.F. Mark	Ordinary Mechanical Properties				Condition (As-cast or As-cast, Soaked at 600° C. for 7½ hr., and air cooled)	Initial Applied Stress, tons/in. ²	Life (days unless otherwise stated)
	U.T.S., tons/in. ²	0.1% Proof Stress, tons/in. ²	Elongation, %	Reduction in Area, %			
OFN 44 (no addn.)	48.3	25.7	22	23	As-cast	27	125
	48.2	25.7	21½	19	Soaked	27	103
OFN 48 (no addn.)	45.1	24.8	13	15½	As-cast	27	65
	45.9	24.3	19	19	Soaked	27	18
OFN 47 (0.03% Zr)					"	27	12 hr.
					"	25.2	1 hr.
					"	25.2	1 hr.
					Soaked	25.2	1 hr.
					"	25.2	65 min.
					"	25.2	4 hr.
OHW 13 (0.08% Ti)	46.3	25.1	18½	20	Soaked	27	5 min.

and manganese. In agreement with the findings of Bailey,¹ the presence of iron and manganese increases the resistance to delayed fracture (cf. Tables IV and VI). In these complex alloys the zirconium and titanium additions had an adverse effect on their resistance to this type of failure.

IV.—DISCUSSION OF RESULTS

It has been suggested² that the susceptibility to intercrystalline flow and fracture in aluminium β -

brasses is a result of the hardening effect of aluminium and of the tendency for aluminium and/or zinc to concentrate at the grain boundaries. The results reported here show that very small amounts of another element, which has a high melting point and whose size-factor is "unfavourable", can give considerable improvement. It is considered unlikely that these small additions would have much effect on the mechanical properties of the grains, and so the improvement is presumably due to their effects on grain-boundary properties. These addition elements would be expected to segregate to the grain boundaries² and there is some microscopical evidence that zirconium does so. Such grain-boundary concentrations could affect both the viscous flow at grain boundaries and the fracture process. The mechanism of the improvement in intercrystalline flow and fracture is, however, not clear.

It is interesting to note that the improvement was very much better for the wrought than for the cast materials, possibly because the wrought alloys had a better chance to reach equilibrium. The results also show that the time to fracture of the cast aluminium β -brasses containing iron and manganese is greater than for the ternary aluminium β -brasses and that zirconium and titanium additions impair the performance of the complex alloys.

ACKNOWLEDGEMENTS

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REFERENCES

1. A. R. Bailey, *Metal Ind.*, 1952, **80**, 519.
2. E. C. W. Perryman, *J. Inst. Metals*, 1954-55, **83**, (8), 369.
3. R. Eborall, unpublished work.
4. R. J. L. Eborall and E. C. W. Perryman (to British Non-Ferrous Metals Research Association), Brit. Patent No. 683,122, 1952.

By D. SUMMERS-SMITH,† B.Sc., Ph.D., A.R.T.C., MEMBER

SYNOPSIS

The solubility of uranium in tungsten and that of tungsten in uranium have been investigated in arc-melted alloys by X-rays, dilatometry, and metallography. At 1000° C., the solubility of tungsten in γ -uranium is about 0.9 ± 0.3 at.-%; that of uranium in tungsten about 0.1 at.-%. The small influence of tungsten on the uranium transformation temperatures suggests that the solubility of tungsten in α - and β -uranium is very slight. These results confirm the work of Schramm, Gordon, and Kaufmann (*Trans. Amer. Inst. Min. Met. Eng.*, 1950, **188**, 195).

I.—INTRODUCTION

ACCORDING to Schramm, Gordon, and Kaufmann,¹ the solubilities of tungsten in uranium and uranium in tungsten at elevated temperatures are probably each less than 1 at.-%. No intermediate phases occur, and tungsten has little effect on the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ uranium transformation temperatures.

Continuous b.c.c. solid solutions are formed between β -titanium and γ -uranium,² β -zirconium and γ -uranium,³ and niobium and γ -uranium;⁴ whereas γ -uranium dissolves a maximum of approximately 43 at.-% molybdenum at 1280° C.⁵ and a maximum of 12 at.-% vanadium at 1040° C.⁶ The transition metals of Groups IV, V, and VIa all have b.c.c. structures and have favourable size-factors with respect to uranium, except for vanadium, which is borderline, and chromium, for which the size difference is 17%. It is thus very surprising that the solubilities of tungsten and tantalum (which has also been investigated by Schramm *et al.*¹) in γ -uranium are so restricted. For this reason the mutual solubilities of γ -uranium and tungsten have been re-investigated.

II.—EXPERIMENTAL PROCEDURE

1. PREPARATION OF THE ALLOYS

The uranium, supplied by the Atomic Energy Research Establishment, Harwell, had a purity considered to be better than 99.95%. The tungsten was in the form of H.S. spectrographic standard rods supplied by Johnson, Matthey and Co., Ltd., who claim a purity above 99.99%, the only significant impurity being molybdenum (estimated to be about 0.01%).

The alloys were prepared by arc-melting on a water-cooled copper hearth under an atmosphere of purified argon. Although satisfactorily homogeneous tungsten-rich alloys could be prepared by melting

the appropriate amounts of the pure metals, uranium-rich alloys could not be obtained in this way, owing to the difficulty of dissolving small quantities of tungsten in liquid uranium.

A series of alloys was therefore prepared from a 50 at.-% tungsten alloy by reducing the tungsten content to approximately 3 at.-% in five stages by melting the alloy with successive additions of uranium. At each stage the alloy was broken up and remelted several times until metallographic examination showed it to be homogeneous. The final 3 at.-% tungsten alloy was used to make up alloys in the range 0–3 at.-% tungsten. Alloys for dilatometric examination were cast into suitable rod form in a groove in the copper hearth of the arc furnace.

2. ANALYSIS OF THE ALLOYS

The alloys were analysed by precipitating the oxides and determining colorimetrically whichever metal was in lower concentration—a procedure developed at A.E.R.E. Results were accurate to approximately 5% of the amounts present.

Three tungsten-rich and four uranium-rich alloys were analysed chemically for uranium and tungsten, respectively. These included the compositions bracketing the terminal solubilities.

III.—EXPERIMENTAL RESULTS

1. THE SOLUBILITY OF TUNGSTEN IN γ -URANIUM

A series of alloys containing up to 10 at.-% tungsten was examined after annealing for 24 hr. at 1000° C. and water-quenching. They were also examined after being cold rolled 20% and annealed for 24 hr. at 1000° C., and again after a repetition of the cold-working and heat-treatment cycle. In the cold-worked and annealed samples, tungsten could be detected in a 1.19 at.-% tungsten alloy, but not in a 0.65 at.-% tungsten alloy. As cast these alloys contained free tungsten in dendritic form; after cold

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rolling and annealing, the tungsten was broken up into discrete, rounded particles.

2. THE SOLUBILITY OF URANIUM IN TUNGSTEN

A series of alloys containing up to 10 at.-% uranium was examined by X-rays and metallography after annealing for 1 hr., 8 days, and 2 months at 1000° C. and water-quenching. The alloy richest in tungsten contained 0.35 at.-% uranium; even after the longest anneal free uranium could be clearly detected metallographically in this specimen.

The lattice parameters of the alloys after various annealing treatments are given in Table I.

TABLE I.—*Lattice Parameters (in kX) of Tungsten-Rich Alloys Quenched from 1000° C.*

Uranium, at.-%	Time of Anneal at 1000° C.		
	1 hr.	8 days	2 months
10	3.1588	3.1587	3.1587
5	3.1589	3.1586	3.1588
3	3.1586	3.1588	...
2	3.1588	3.1588	3.1589
1.5	...	3.1585	3.1587
1.05 *	...	3.1586	3.1587
0.62 *	3.1589
0.35 *	3.1589	3.1587	3.1588
0	3.1585	3.1586	...

* Analysed compositions; remainder nominal.

There is a slight, but probably significant, increase in tungsten parameter from 3.1586 kX for the pure metal to a mean value of 3.1588 kX when alloyed with uranium. Assuming Vegard's law to be applicable, this would correspond approximately to a solubility of 0.1 at.-% uranium in tungsten.

3. THE EFFECT OF TUNGSTEN ON THE URANIUM ALLOTROPIC TRANSFORMATIONS

The solid-state transformations in uranium-rich alloys were examined by dilatometry, using heating and cooling rates of 1° C./min.; the dilatometer used has been described elsewhere.³ The transformation

temperatures are shown in Table II, together with the values obtained for two uranium specimens.

TABLE II.—*Transformation Temperatures (°C.) of Uranium-Rich Alloys.*

Tungsten, at.-%	$\alpha \rightleftharpoons \beta$		$\beta \rightleftharpoons \gamma$	
	Heating	Cooling	Heating	Cooling
0.1	671	639	774	760
0.3	674	645	774	758
0.5	669	637	773	757
1.0	672	647	776	760
1.5	672	643	776	759
2.0	672	642	778	759
10	670	646	773	760
Uranium	667.5 ± 0.5	645 ± 6	773 ± 2	761 ± 2

There is probably a slight increase in both transformation temperatures, but it is very small and is somewhat masked by the hysteresis which occurs in each transformation.

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REFERENCES

1. C. H. Schramm, P. Gordon, and A. R. Kaufmann, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, **188**, 195.
2. A. G. Knapton, unpublished work.
3. D. Summers-Smith, *J. Inst. Metals*, 1954-55, **83**, (6), 277.
4. P. C. L. Pfeil, unpublished work.
5. P. C. L. Pfeil, *J. Inst. Metals*, 1950, **77**, 553.
6. H. A. Saller and F. A. Rough, *Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197**, 545.

THE INTERACTIONS OF STATIC STRESS AND CORROSION WITH ALUMINIUM ALLOYS*

1609

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SYNOPSIS

Existing knowledge from laboratory experiments and service experience on the susceptibility of aluminium alloys to stress-corrosion and on methods of protection is reviewed, with particular reference to practical implications. It is important to distinguish between alloys that are liable to fail by stress-corrosion and those that are not. Precautions can then be taken in appropriate cases, and unnecessary precautions and restrictions avoided in others. If precautions are taken with the few alloys that are susceptible, the risk of stress-corrosion failure in service is extremely small.

I.—INTRODUCTION

Most of the metallic elements give some alloys which are liable to failure by stress-corrosion under certain conditions.¹ The appropriate conditions vary considerably for the different metals, and it seems doubtful whether a single satisfactory and detailed theory can be developed for the mechanism of all stress-corrosion. For simplicity and clarity the present paper is confined to the consideration of aluminium-base alloys.

Its primary purpose is to try to obtain a true perspective of stress-corrosion from the practical point of view in the aluminium alloys ‡ at present standardized in this country. The term "static stress" is used in the title to make it clear that fatigue conditions are not considered in detail. Some variation in stress may occur without causing departure from the intercrystalline fracture which is characteristic of stress-corrosion failure in aluminium alloys; the transcrystalline fractures characteristic of corrosion-fatigue of aluminium alloys are outside the scope of the paper.

Varied interpretations of the term "stress-corrosion" appear to have been responsible for confusion which has arisen in this field, so that its definition must be considered first.

II.—DEFINITION OF STRESS-CORROSION

It seems most important to differentiate between (a) intercrystalline attack which can reduce mechanical strength, but is itself relatively unaffected by service loads, and (b) stress-corrosion which is a true conjoint action of stress and corrosion, since the latter is of a more insidious character and narrows the range of effective precautions against failure. The following definition of stress-corrosion, published in 1945,² having received no adverse comment, is now widely

adopted in this country, and is used in the present paper:

"The term 'stress-corrosion' implies a greater deterioration in the mechanical properties of the material through the simultaneous action of a static stress and exposure to corrosive environment than would occur by the separate, but additive, action of those agencies."

It is, therefore, not sufficient simply to expose a metal simultaneously to stress and corrosion in order to assess its susceptibility to stress-corrosion. Comparable specimens must be exposed to the same corrosion conditions but without stress, and stress-corrosion is demonstrated only if the stressed specimens suffer the greater deterioration. Failure of a specimen when simultaneously exposed to stress and corrosion can occur simply because weakening of the specimen by corrosion reduces the residual strength until it is less than the load applied. This is particularly true of intercrystalline corrosion because of the notch effect which results from this type of attack.

It is also desirable to subject comparable specimens to a similar stress while protected from corrosion. For example, titanium specimens cut transversely to the rolling direction were loaded to 90% of the 0.2% proof stress in an urban atmosphere; they broke in 10–14 days, the failure being attributed to creep and not to stress-corrosion.³ Although aluminium alloys generally show much less creep than titanium, precautions against confusion by this factor seem advisable in stress-corrosion tests on aluminium alloys. If stressing of control specimens without corrosion is impracticable, the difficulty can be safely avoided by limiting the maximum stress to the commonly used testing level of 75% of the 0.1% proof stress of the particular metal.

Simple exposure to stress plus corrosion, without control specimens exposed to stress or corrosion alone,

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‡ When the term "aluminium alloys" is used generally in this manner, it may be taken to include the various grades of pure aluminium.

may well provide an adequate experimental method when the metal is known to be susceptible to stress-corrosion. For example, this simple technique may be used for exploratory tests, especially when investigating variations in the corrosive environment.

The above principles apply mainly to the investigation of stress-corrosion in laboratory tests or field trials. Investigation of suspected service failures is much more difficult. It is not possible to be sure that such failures in aluminium alloys are due to stress-corrosion unless positive evidence, under each of the following heads, is obtained.

(1) The fracture and subsidiary or branching cracks are intercrystalline, except perhaps for the final purely mechanical rupture (Fig. 3, Plate LIX). There should be few branch cracks and the subsidiary cracks should be relatively isolated compared with the network of intercrystalline penetration (Fig. 2, Plate LIX) which can occur in the absence of stress. This network is often partly localized.

(2) The metal must be known to have been subject to tensile or bending stresses while exposed to corrosion in service. Such stresses may be internal, e.g. residual from fabrication, or external due to service conditions.

(3) The metal in the condition in which it was used must be known to be susceptible to stress-corrosion. If this information is not available, laboratory tests should be made for the purpose, preferably on sound metal cut from the failed part.

In some instances the breaking up or distortion of the crystals during previous working of the metal may give rise to difficulty in ascertaining whether the cracks are intercrystalline in character. The principle of paragraph (3) should then be applied, i.e. laboratory tests should be made to ascertain the detailed character of stress-corrosion cracks formed in the laboratory in a simple cut from the failed member.

III.—MECHANISM OF FAILURE

In polyphase cast aluminium alloys there may be sufficient electrochemical difference between two phases to concentrate corrosion of the alloy to some degree on the more anodic phase. An example of this is shown in Fig. 1 (Plate LIX). In wrought aluminium alloys, however, this selective attack of the structure is almost invariably intercrystalline, as shown in Fig. 2, Plate LIX, phases at or near the grain boundary being attacked preferentially.⁴⁻⁶ Dubietz exists with cold-worked metals where the grain structure is too broken for one to be certain of the relation between corrosion and structure. Intercrystalline attack may be expected to produce a more serious stress concentration than, for example, the structural attack of Fig. 1 or the pitting of pure aluminium. Consequently mechanical testing of metal showing intercrystalline attack usually reveals a greater deterioration in mechanical properties in relation to the loss of metal by corrosion. If the load is applied while

the metal is exposed to corrosion, then the strength may be sufficiently reduced by this attack to cause failure under the applied load, the rapid fracture being of the normal transcrystalline type. If the alloy is not susceptible to stress-corrosion, it is immaterial, with regard to both type of fracture and the load required, whether the stress is applied during or after exposure to corrosion. In the absence of complicating factors, such as galvanic effects or extreme acidity or alkalinity of the corrosive environment, the corrosion/time curve is then of the asymptotic form illustrated in Fig. 4.⁷ The "induction period" or delay in the onset of corrosion indicated in Fig. 4 may vary considerably with the metal and conditions of exposure.

If the metal is susceptible to stress-corrosion, then the simultaneous application of stress accelerates the

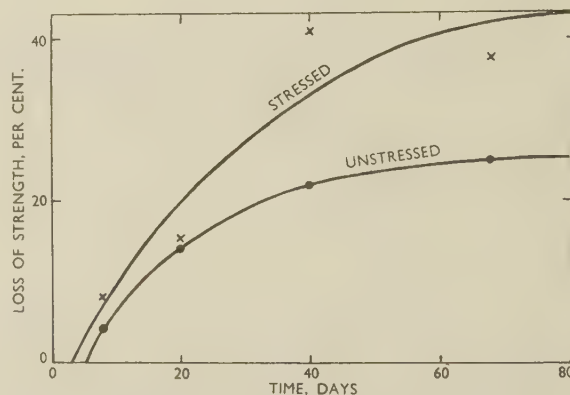


FIG. 4.—Effect of Stress on the Corrosion in Salt Spray of Inefficiently Quenched H14 T Alloy.

rate of intercrystalline penetration. This effect is small during the early stages of exposure, so that initially the corrosion/time curve may still be of the asymptotic form. As the rate is accelerated, however the form of the curve is radically changed, as shown in the smooth curve of Fig. 5, and penetration eventually proceeds at such a rapid rate that the ultimate fracture is largely intercrystalline (owing to stress-corrosion) and only a small proportion of it is transcrystalline (due to the final mechanical failure). Moreover, this intercrystalline failure takes the form of a fairly isolated crack (*A*, Fig. 3, Plate LIX) as distinct from the network of intercrystalline corrosion shown in Fig. 2; the final mechanical failure is shown at *B* in Fig. 3. Thus the major effect of stress in stress-corrosion failure is concentrated in the later stage of the failure, but with the relatively rapid failure which can be obtained in the laboratory the earlier asymptotic portion of Fig. 5 may not be observed.^{6, 8, 9}

While many aluminium alloys are susceptible to intercrystalline corrosion to various degrees, relatively few of them are susceptible to stress-corrosion (see Section VI), and Dix's theory⁴ requires some elaboration to explain this.¹⁰ The asymptotic form of corrosion/time curve (Fig. 4) experienced with aluminium alloys under many conditions is attributed

to the gradual formation of a highly protective and adherent oxide film on a reactive metal.¹¹ This applies even to alloys showing intercrystalline attack, so that the film appears to form in the intercrystalline crevices. When the stress concentration at the notch formed by the tip of such attack exceeds the proof stress, local deformation of the metal occurs, causing rupture of the oxide film at that point. This allows corrosion to proceed again at the more rapid rate, particularly since the exposed metal is anodic to the adjoining film-covered metal.⁴ The rate of attack gradually decreases, however, as the film re-forms. If the corrosion once more gives rise to a sufficient stress concentration before the oxide film has become adequately protective, local deformation recurs; penetration thus proceeds at an increasing rate to give the broken curve of Fig. 5. If the corrosion rate is

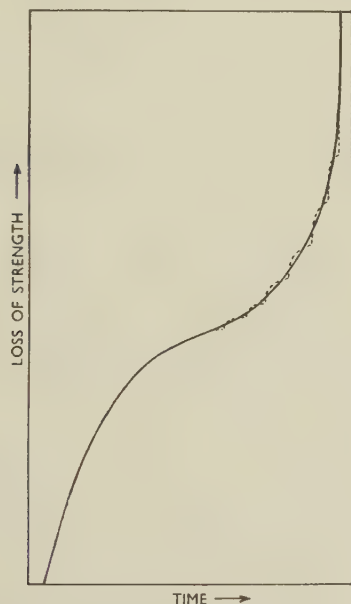


Fig. 5.—Idealized Corrosion/Time Curves Leading to Stress-Corrosion Fracture.

sufficiently reduced before a dangerous stress concentration is reached, rupture of the film is prevented, and the corrosion/time curve retains the asymptotic form of Fig. 4. The results obtained by Gilbert and Hadden¹² and Logan¹³ appear to support this theory, so that the detailed curve of Fig. 5 is strictly the stepped one.

On this view, the extension from susceptibility to intercrystalline corrosion to susceptibility to stress-corrosion depends largely upon the film-forming properties and deformability of the alloy. Intercrystalline corrosion is attributed solely to electrochemical corrosion, the different phases of the alloy at the grain boundaries constituting anodes and cathodes. The inherent solution potentials of these phases are primarily responsible for the potential difference between the anodes and cathodes, but the effect may be modified (e.g. increased) by differences in the protective value of the film formed on the different phases. The possibility of converting intercrystalline

corrosion to stress-corrosion, by applying stress during exposure to corrosion, appears to require a combination of several factors in the particular alloy, as follows:

(1) A rate of intercrystalline penetration by corrosion which is high relative to the rate of protective-film formation. The magnitude of the potential difference between the anodic and cathodic phases and other characteristics, such as relative size, of these phases are no doubt important in this respect.

(2) The extent of the local deformation of the metal which occurs if and when the stress concentration reaches the critical value, and the distribution of that deformation between the different phases.

(3) The properties and especially the extensibility of the protective film on the different phases.

The combination of (2) and (3) will probably determine whether film rupture occurs and whether it occurs on such an alloy phase as to give maximum acceleration of intercrystalline penetration. It should be noted that this paragraph involves much speculation on the causes of the observed fact that aluminium alloys can be susceptible to intercrystalline corrosion without being susceptible to stress-corrosion: there is scope for experimental work on this question.

IV.—ENVIRONMENT

Chlorides and moderately acid conditions¹² are most liable to cause intercrystalline corrosion or stress-corrosion of aluminium alloys. Perryman and Hadden⁶ found that the stress-corrosion of an aluminium-7% magnesium alloy in a susceptible condition increased with increasing sodium chloride content up to about 9%. With extreme acidity general attack is more likely to occur, and serious intercrystalline attack or stress-corrosion is not then observed, but the moderate acidity of a mixed marine-industrial type of atmosphere provides very severe conditions. Humidity is an important factor and appears to have its maximum effect at about 80% relative humidity in salt-spray tests.⁶

Stress-corrosion of susceptible alloys can, however, occur in much milder conditions. Indeed, laboratory tests under moderately humid conditions, but with very little pollution of the atmosphere, have given stress-corrosion (of abnormally aged 5L3 alloy) with extremely fine and isolated cracking, which was difficult to detect by visual inspection. Normally, however, the stresses present cause sufficient mechanical widening of the crack to render it visible to close inspection, and stress-corrosion in service is normally associated with more corrosive environments.

Oxygen is necessary for stress-corrosion, and penetration can be stopped and re-started at will in the laboratory by control of the oxygen supply.^{6, 12}

V.—STRESS CONDITIONS

The stress conditions used in laboratory tests may be divided into two main types, according to whether

they approximate to constant-strain or constant-load conditions. The former approximate to internal stresses from production and to fabrication stresses, e.g. misalignment of rivet holes, while the latter approximate to service stresses. These stresses may be additive. The constant-load type of conditions is

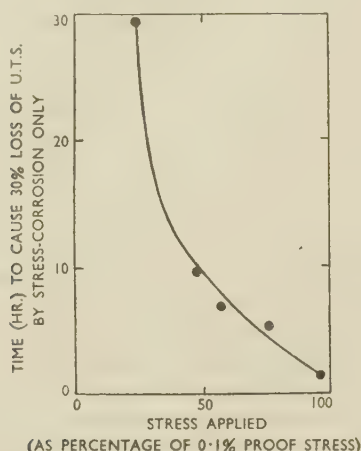


FIG. 6.—Example of Effect of Stress Level on Rate of Stress-Corrosion. (NW 7, abnormally aged.)

the more effective in causing stress-corrosion in the laboratory, but in many applications, e.g. in aircraft, they reach high values only for short periods. In general, high internal stresses arising from fabrication and assembly predominate as causes of stress-corrosion failure in service.⁴ The continuous application of high constant loads in laboratory tests can make them more severe in relation to service conditions than they appear to be at first sight. Reference has already been made to other reasons for not using test stresses above 75% of the proof stress of the actual metal tested. Tensile stresses are usually more severe than bending stresses, while compressive stresses have little if any effect.^{6, 14}

The rate of stress-corrosion decreases markedly with

reduction in stress, and there appears to be a limiting stress (the value of which will no doubt depend on the alloy and its condition) below which significant stress-corrosion does not occur. An example is shown in Fig. 6 for aluminium-7% magnesium alloy intermittently immersed in 3% sodium chloride solution of pH 6.¹⁵

The orientation of the stress in relation to the wrought grain structure is important, stress-corrosion being more likely to occur when the stresses are transverse to the elongated grain structure.^{5, 16} Particular attention should be paid to this when machining complicated parts from extrusions or forgings of susceptible alloys.

VI.—COMPOSITION AND CONDITION OF THE ALLOY

The author is not aware of any reliable evidence of stress-corrosion of the metals listed in Table I, in any conditions occurring in practice; this also applies to super-purity aluminium, which is not at present included in British Standards. No reliable evidence of stress-corrosion of cast aluminium alloys appears to have been published, and Table I is therefore confined to wrought alloys.

Standardized British alloys on which there is definite or suggestive evidence of some degree of stress-corrosion are considered below. Stress-corrosion susceptibility has been observed much more frequently in laboratory experiments than by actual service experience, and the two sources of information are therefore considered separately.

1. LABORATORY TESTS AND FIELD TRIALS

Among the alloys which are not normally heat-treated for the development of the required mechanical properties, stress-corrosion has been observed only in the aluminium-magnesium alloys of high magnesium content; moreover, the latter are not susceptible in the as-manufactured condition.⁶ The

TABLE I.—*Wrought Aluminium Alloys Not Shown to be Significantly Susceptible to Stress-Corrosion.*

Alloys Specified in B.S. 1470-6	Composition, %								Cladding
	Si	Fe	Cu	Mn	Mg	Zn	Cr	Al †	
1A	0.15	0.15	0.02	99.8	...
1B	0.3	0.15	0.05	0.05	99.5	...
1C	0.5	0.7	0.1	0.1	99.0	...
N 2	10.0-13.0	0.6	0.1	0.5
N 21	4.5- 6.0	0.6	0.1	0.5
N 3	0.6	0.75	0.15	1.0-1.5
N 4	0.6	0.75	0.15	...	1.75-2.25	...	0.5
N 5	0.6	0.75	0.15	1.0	3.0-4.0	0.1	0.5
H 9	0.3-0.7	0.6	0.15	...	0.4-0.9	0.1
H 10	0.75-1.3	0.6	0.15	1.0	0.4-1.5	0.1	0.5
HC 14 *	0.7	0.7	3.5-5.0	0.4-1.2	0.4-1.2	1B
HC 15 *	0.9	1.0	3.5-4.8	1.2	0.85	...	0.3	...	1B
D.T.D. 687 * . .	0.5	0.5	1.5	0.3-1.0	2.0-3.5	4.5-6.5	0.5	...	Al-1% Zn

N.B.—It does not follow that alloys not listed here are subject to stress-corrosion under all conditions of usage.

* Resistance to stress-corrosion dependent on cladding.

† Minimum: other single figures are maxima.

actual percentage of magnesium required to introduce susceptibility is doubtful, but is probably of the order of 5.0%. Most of the laboratory work has been concerned with the aluminium-7% magnesium alloy (N 7).^{*} When this alloy is in a heterogeneous condition, such that a continuous film of β precipitate is formed at the grain boundary, it is highly susceptible.⁶ This condition results from ageing the solid solution at moderately elevated temperature, for example 24 hr. at 125° C. or a much longer time at tropical temperature, especially if the ageing is preceded by cold work. More prolonged ageing agglomerates the precipitate and thereby progressively reduces susceptibility, but this reduction is attained before agglomeration can be observed in microsections. Grain-boundary β precipitation in the aluminium-magnesium alloys listed in Table I increases susceptibility to intercrystalline attack, but has not been found to introduce susceptibility to stress-corrosion. Metcalfe¹⁷ tested lap joints of Duralumin sheet with alloy rivets containing 4.65-4.90% magnesium and found some loss of shear strength under stress conditions when the rivets were driven as received, and especially after ageing for 14 days at 70° C., but not after annealing at 350° C. The grain-boundary precipitation in the as-received rivets was considered to be abnormal. He concluded that, even after 12 months' exposure to stress and sea-water spray, the reduction in shear strength of the rivets was negligible. Smith¹⁸ pointed out the danger of excessive cold work occurring, and even of a crack being formed at the junction of the head and shank of rivets during driving, if the technique was not correct. It is possible that the failures were due to localization of intercrystalline corrosion by heterogeneous structure and the presence of the crack, especially since it was admitted that the stress conditions in the stress-corrosion tests conformed to commercial practice rather than to good testing technique: evidence of the importance of driving cracks has been obtained in more recent corrosion tests with large rivets.¹⁹ It is significant that, in his terminal discussion of results, Metcalfe referred to intercrystalline corrosion and not to stress-corrosion.

Walkiden¹⁹ has made stress-corrosion tests on two 25-S.W.G. aluminium-magnesium alloy wires containing, respectively, magnesium 3.85, manganese 0.76% and magnesium 4.85, manganese 0.32%. The hard-drawn wires were heated for 2 hr. at 175° C. and with some samples this was followed by 24 hr. at 125° C. Triplicate specimens were then loaded in tension to 75% of the 0.1% proof stress. These and unstressed control specimens were sprayed twice daily with 3% salt solution. None of these fine wires broke during exposure for 600 days. When they were removed, the one with the lower magnesium content showed no indication of stress-corrosion, while there was only a moderate effect with the other (4.85% magnesium) as shown in Table II. Jones⁸ found strained and artificially aged aluminium-4.8%

magnesium alloy wires susceptible to stress-corrosion at stresses greater than 35% of the 0.1% proof stress when submitted to intermittent immersion in 3% sodium chloride solution buffered to a pH of 6, but the susceptibility was much less than for the aluminium-6.9% magnesium alloy after similar treatment.

The aluminium-10% magnesium casting alloy (B.S. 1490, LM 10) has been found to fail more readily under stress-corrosion conditions when slowly cooled after solution-treatment (which also results in inferior mechanical properties) than when heat-treated within the range of commercial practice.²⁰

TABLE II.—*Stress-Corrosion Tests on Aged NW 6 Alloy.*

Ageing Treatment	Loss of U.T.S., %	
	Unstressed	Stressed
2 hr. at 175° C.	11	21
2 hr. at 175° C. and 24 hr. at 125° C.	10	44

No data were provided on the behaviour of these specimens when exposed to corrosion in the absence of stress, so that the tests did not provide conclusive evidence as to whether stress-corrosion had occurred even with the abnormal condition of these castings.

The aluminium-copper-magnesium alloys (H13 and H14) are not susceptible to stress-corrosion when efficiently quenched and naturally aged; even with very inefficient quenching there is only slight susceptibility, as shown in Fig. 4, although they are then strongly susceptible to intercrystalline corrosion. With abnormal thermal treatment, such as stoving after painting, they are markedly susceptible, especially if such thermal treatment is preceded by cold work.

The aluminium-copper-magnesium-silicon alloy in the solution-treated and naturally-aged condition (H15 W) shows susceptibility to stress-corrosion only if inefficiently quenched.⁵ When maximum mechanical properties are developed by artificial ageing (to give H15 WP) or when the solution-treated alloy is subjected to a moderately elevated temperature, and especially after cold work (as, for example, in the stoving of formed and painted parts), then serious stress-corrosion can occur.

The aluminium-zinc-magnesium alloys, which give the highest mechanical properties, are susceptible to stress-corrosion, but this is minimized in the standardized alloys by the addition of copper and manganese, or chromium (e.g. D.T.D. 683).

To sum up, laboratory tests have indicated a serious risk of stress-corrosion in N7 (only when aged, for example at tropical temperatures), H14 T (only when carelessly heated after the normal solution-treatment), H13 T and H15 W (only when inefficiently quenched), H15 WP, and the D.T.D. 363/D.T.D. 683 type. There may be a very slight risk with N 6 when it has

* The nomenclature of B.S. 1470-6 is used where applicable.

been aged, for example, at tropical temperature. The general inference from these conclusions is that the risk of stress-corrosion of practical importance is introduced in the development of the highest mechanical properties by alloying and heat-treatment.

2. SERVICE EXPERIENCE

No examples of stress-corrosion failure of aluminium alloy castings in service are known to the author; this may be due partly to the relatively low stresses to which they are normally subjected. The experience of the Royal Aircraft Establishment is still as given by George and Chalmers.^{20, 21} Stress-corrosion failures in British aircraft are extremely rare, and have been observed only in the wrought forms of aluminium alloys. Those containing a high percentage of zinc (e.g. D.T.D. 363) or 2½% copper, 1½% nickel, 1% magnesium, and 1% iron (H12) were stated to be highly susceptible. Aluminium-magnesium rivets containing 5% magnesium failed by fracture at the junction of head and shank when used on aircraft in tropical service. George and Chalmers considered the fracture to be due to stress-corrosion, but Metcalfe,¹⁷ who investigated them in more detail, found that they contained 4.6% magnesium, and that the cracking was less localized and less marked than in rivets containing 7.0% magnesium and, in the absence of conclusive evidence, attributed the fracture to "intercrystalline corrosion, probably accentuated by stress". Aluminium-5% magnesium (N6) aircraft rivets are not normally used now for jointing aluminium alloys, mainly because of inadequate shear strength. No stress-corrosion failures have been experienced with wrought aluminium-magnesium alloys containing less than 4.5% magnesium or with aluminium-magnesium alloy castings. D.T.D. 363-type alloys were used during the war with only anodizing followed by painting as protection, but no case of failure in service by stress-corrosion is known. German metallurgists, who often have a wider interpretation of the term "stress-corrosion" than is used in this paper, examined crashed British aircraft and stated that they found no failures which could be attributed to stress-corrosion.

The suggestion has been made that stress-corrosion has been a contributory factor in some failures of D.T.D. 683 (D.T.D. 363-type) forgings and in an isolated case in D.T.D. 364 forgings (H15 WP), but decisive evidence is not available. Cracks in American aircraft extrusions and forgings in 24S-T4 (H14 T type except for high magnesium content) and in H15 WP and D.T.D. 683 types of alloys have been attributed to a stress-corrosion, although it was acknowledged that the evidence was not conclusive.²²

There appears to have been only one failure in naval aircraft which could be attributed to stress-corrosion, and this occurred in components fabricated from an aluminium-copper-magnesium-silicon-nickel alloy (H 12). They were anodized and painted only and failed by cracking after 3 years' service. No stress-corrosion failures of aluminium-5% magnesium rivets

have been observed in naval aircraft.²³ Thousands of tons of aluminium-magnesium alloys containing up to 5.5% magnesium have been used during and since the recent World War in the construction of naval ships; the alloys were largely in a cold-worked condition, and many of the ships spent a considerable time in tropical waters. Laboratory tests indicate that some susceptibility would be developed in these circumstances, but in fact no stress-corrosion failures have been observed. Aluminium-7% magnesium alloy plate used in ships has given serious trouble which may have been due to stress-corrosion.

To sum up, there is some evidence of isolated service failures due to stress-corrosion in the D.T.D. 363, D.T.D. 683, and H12 types of alloy and possibly in H15 WP and N7. There have possibly been stress-corrosion failures of N6 rivets in aircraft, but naval experience of N6 alloy in various forms in aircraft and ships has been entirely satisfactory with respect to stress-corrosion. There have been no stress-corrosion failures in casting alloys or in any of the wrought alloys given in Table I. Finally, it should be noted that all the alloys indicated as involving a serious risk of stress-corrosion according to laboratory tests have been used in service for stressed members and often in circumstances where protection, such as cladding, could not be provided, but that failure of aluminium alloys in service by stress-corrosion is very rare.^{5, 20}

TABLE III.—*Wrought Aluminium Alloys Not Normally Requiring Protection against Stress-Corrosion.*

(Additional to Table I)

Alloys Specified in B.S. 1470-6	Composition, % *					
	Si	Fe	Cu	Mn	Mg	Cr
N 6	0.6	0.75	0.15	1.0	4.5-5.5	0.5
H13 T	0.7	0.7	1.5-3.0	0.5	0.2-0.5	
H14 T	0.7	0.7	3.5-5.0	0.4-1.2	0.4-1.2	
H15 W	0.9	1.0	3.5-4.8	1.2	0.85	0.3

* Single figures indicate maxima.

Alloys which have been widely used (in the given condition of heat-treatment) without protection such as cladding or metal spraying are listed in Table III. Their protection against other corrosion effects, e.g. by painting, may be desirable, depending on the alloy and environment.

VII.—PROTECTIVE MEASURES

It is common practice with engineers to make a "corrosion allowance", particularly for steel, when deciding on the thickness of metal required. Increase in thickness is particularly advantageous when the corrosion/time curve is asymptotic.²⁴ On the evidence at present available, however, with aluminium alloys subject to stress-corrosion the advantage of increase in initial thickness is limited to the corresponding reduction in stress per unit cross-sectional area for a given load.

Every endeavour should be made to avoid high stresses resulting from fabrication and assembly. With large cross-sectional areas in alloys to be heat-treated, it may be necessary to reduce the quenching rate from solution-treatment (e.g. by quenching in hot water) in order to reduce internal quenching stresses; since this may introduce or increase susceptibility to intercrystalline corrosion with some alloys, it is evidently necessary to consider cases individually. Internal stresses due to cold work can be minimized by forming heat-treatable alloys in the annealed condition; subsequent solution-treatment, required to give the appropriate mechanical properties, will then relieve the forming stresses. Otherwise, thermal stress-relieving treatments are not usually applicable to wrought aluminium alloys. Promising results have been obtained in the laboratory^{6, 25} by partially neutralizing tensile stresses in the surface by means of compressive stresses induced, for example, by shot-peening. Such methods must be used with caution, however, since the induced surface stresses may possibly accelerate ageing of the metal to a condition which is more susceptible to stress-corrosion, as for example with the binary alloys of high magnesium content. Careful design of parts to avoid high local stresses and stress-raisers is evidently very important.

The most effective protection based on service experience so far consists of the pure aluminium cladding rolled on to aluminium-copper-magnesium and aluminium-copper-magnesium-silicon alloys (to give HC14 and HC15, respectively). The author is not aware of any case of stress-corrosion of these alloys, in the laboratory or in service, where they have been adequately clad. The same is true of the aluminium-1% zinc alloy cladding rolled on to the aluminium-zinc-magnesium-copper alloy (D.T.D. 683) to give D.T.D. 687, although service experience is less extensive (i.e. about 10 years) with this metal than with the HC14 or HC15 type of alloy. The copper content of the H14 and H15 alloy ensures that the pure aluminium cladding of HC14 and HC15 is adequately anodic to the core, but owing to the high zinc content of the D.T.D. 683 type of alloy an aluminium-1% zinc alloy is specified in D.T.D. 687 to give an anodic cladding. It should be noted that in such cases the cladding thickness is a fixed percentage of the total metal thickness. Consequently, if very thin clad sheets are used, the cladding will be so thin as to allow serious diffusion of copper into it during the thermal treatments necessary in the course of production, with consequent reduction in the protection provided to the underlying strong alloy.

With H15 extrusions and forgings, a sprayed coating of pure aluminium should give adequate protection, since it has been shown to give adequate protection to H15 extrusions when they are exposed to corrosion in the absence of stress,²⁶ while laboratory tests^{4, 9} and experience with rolled-on cladding shows that stress-corrosion is prevented by cathodic protection. Stress-corrosion tests now proceeding on sprayed aluminium coatings on HS 15 support this

view.¹⁶ Sprayed coatings of aluminium-base alloys would be expected to give adequate protection to other extrusion and forging alloys, provided the alloy coating is of a suitable composition to render it appropriately anodic to the core alloy. Thus Hooker and Waisman²² obtained efficient protection against stress-corrosion of the D.T.D. 683 type of alloy by intact sprayed coatings of aluminium-1% zinc alloy. Gaps machined in the coating resulted in eventual failures in some cases, but the results suggested that the direction of machining relative to the direction of stressing was an important factor in causing this loss of protection. Hence these latter tests did not provide reliable information on behaviour when part of the coating is *corroded away*.

For many conditions of exposure no further protection is necessary over the cladding or sprayed coating, but under very severely corrosive conditions these coatings may be eventually corroded away over areas too large to permit sacrificial protection of all the exposed core alloy. For exceptionally long life under such conditions, therefore, further protection may be provided, for example by painting. Anodizing is not recommended for this purpose (even as a preparation for painting), since it is likely to interfere with the sacrificial protection of the core. The other methods of ensuring good paint adhesion, such as the use of a pre-treatment or "wash" primer, can be employed (although this is usually unnecessary with sprayed coatings), followed by a full chromate primer, and then a waterproofing top coat. If paint films are not adequately maintained, they can become harmful when deteriorated; where adequate maintenance is not possible, therefore, it is preferable to leave the coating unprotected and to effect local repairs to the coating by metal spraying if and when that becomes necessary. When a cladding or sprayed coating is not employed, anodizing is decidedly advantageous as a preparation for painting, and such a system has given adequate protection on service aircraft as mentioned earlier (Section VI, 2), but this system must be regarded as less reliable than protection relying on anodic metal coatings.²¹ Where susceptible alloys are used in the form of bolts, the overall paint system should be supplemented by chromated jointing compound (D.T.D. 369A) applied to the bolt before insertion.

The sacrificial protection afforded by anodic cladding should also be applicable by separate anodes connected to the susceptible alloy,^{4, 9, 27} although the author is not aware of service experience with this. Conversely, stress-corrosion of a susceptible alloy might be stimulated by contact with a cathodic metal.

VIII.—SUMMARY AND GENERAL CONCLUSIONS

Most aluminium alloys have not shown stress-corrosion failure even though they may be susceptible to intercrystalline corrosion, but the use of alloy

compositions and heat-treatments designed to give the highest mechanical properties tends to result in varying degrees of susceptibility to stress-corrosion. Stress-corrosion failures in service are very rare, and in fact far more stress-corrosion has been observed in the laboratory than in service, partly because the laboratory results have served to minimize the risk of stress-corrosion in service, and partly because laboratory tests have included conditions more severe than those experienced in service. The latter factor is evidently advantageous in providing a safety margin, but care must be taken to ensure that excessive safety margins do not place unnecessary restrictions on the alloys available to the engineer. For example, interference from creep effects can be avoided and better correlation with service experience obtained by limiting the stress in laboratory tests to not more than 75% of the 0.1% proof stress. Tensile stresses have more effect than bending stresses, while compressive stresses have no practical importance: where the

structure of the metal is markedly directional, stresses parallel to that direction are much less harmful than those normal to it. Industrial-marine atmospheres are liable to give the most severe effects, especially at about 80% relative humidity, but quite mild atmospheres may cause serious effects in a markedly susceptible metal.

Thicker metal is advantageous when it reduces the stress per unit area and, in general, much can be done at the design stage to minimize corrosion risks. Rolled-on cladding offers the maximum protection, and sprayed metal coatings appear to be equally effective. Painting has been effective in some applications, especially when preceded by anodizing and supplemented where necessary by suitable jointing compounds.

ACKNOWLEDGEMENT

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REFERENCES

1. H. R. Copson, "The Corrosion Handbook." Edited by H. H. Uhlig, p. 569. 1948: New York (John Wiley and Sons, Inc.); London (Chapman and Hall, Ltd.).
2. H. Sutton, E. A. G. Liddiard, B. Chalmers, and F. A. Champion, *Monthly J. Inst. Metals*, 1945, (Aug.), xxii.
3. F. M. Reinhart, private communication, 1954.
4. E. H. Dix, Jr., *Trans. Amer. Inst. Min. Met. Eng.*, 1940, 137, 11; R. B. Mears, R. H. Brown, and E. H. Dix, Jr., *Symposium on Stress-Corrosion Cracking in Metals (A.S.T.M.-A.I.M.E.)*, 1944, 323.
5. E. H. Dix, Jr., and R. H. Brown, *Metals Handbook (Amer. Soc. Metals)*, 1948, 228.
6. E. C. W. Perryman and S. E. Hadden, *J. Inst. Metals*, 1950, 77, 207.
7. F. A. Champion, *Symposium on Stress-Corrosion Cracking in Metals (A.S.T.M.-A.I.M.E.)*, 1944, 358.
8. E. Lloyd Jones, *J. Appl. Chem.*, 1954, 4, (1), 1.
9. C. Edeleanu, *J. Inst. Metals*, 1951-52, 80, 187.
10. F. A. Champion, *Inst. Metals: Symposium on Internal Stresses in Metals and Alloys*, 1948, 468 (discussion).
11. F. A. Champion, *Metal Ind.*, 1948, 72, 440, 463.
12. P. T. Gilbert and S. E. Hadden, *J. Inst. Metals*, 1950, 77, 237.
13. H. L. Logan, *J. Research Nat. Bur. Stand.*, 1952, 48, 99.
14. W. D. Robertson, *Trans. Amer. Inst. Min. Met. Eng.*, 1946, 166, 216.
15. E. Lloyd Jones, *J. Appl. Chem.*, 1954, 4, (1), 5 (Fig. 4).
16. E. A. G. Liddiard and W. A. Bell, *J. Inst. Metals*, 1953-54, 82, (9), 426.
17. G. J. Metcalfe, *ibid.*, 1946, 72, 487.
18. C. Smith, *ibid.*, 665 (discussion).
19. G. W. Walkiden, unpublished work.
20. G. Meikle, private communication, 1954.
21. C. W. George and B. Chalmers, *Symposium on Stress-Corrosion Cracking of Metals (A.S.T.M.-A.I.M.E.)*, 1944, 345.
22. R. N. Hooker and J. L. Waisman, *Corrosion*, 1954, 10, (10), 325.
23. E. J. Hammersley, private communication, 1954.
24. F. A. Champion, *Metal Ind.*, 1949, 74, 7, 13.
25. S. E. Hadden and E. C. W. Perryman, *Metallurgia*, 1950, 42, 392.
26. F. A. Champion, *Metal Ind.*, 1951, 79, 355, 384.
27. H. J. MacDonald and J. T. Waber, *Symposium on Cathodic Protection (Electrochem. Soc. and Nat. Assoc. Corrosion Eng.)*, 1949, 192.

SPECIFIC-HEAT MEASUREMENTS ON ALUMINIUM-4% 1610 COPPER AND ALUMINIUM-4% COPPER-TIN ALLOYS *

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SYNOPSIS

Measurements of the instantaneous apparent specific heat of aluminium-copper and aluminium-copper-tin alloys on heating showed a heat evolution due to precipitation which, on further raising the temperature, was replaced by a heat absorption due to re-solution. The temperatures at which the maximum rate of heat evolution occurred on heating (corresponding to the maximum rate of precipitation) were :

	Al-4% Cu	Al-4% Cu-0.05% Sn
Quenched	285° C.	200° C.
Quenched and compressed 5%	245° C.	220° C.

The total heat evolved on precipitation was unaffected by the presence of tin or by cold work before testing.

INVESTIGATIONS have shown that very small quantities —of the order of 0.05–0.1 wt.-%—of cadmium, indium, and tin exert a pronounced influence on the response of aluminium-copper alloys to ageing at elevated

Measurements of the instantaneous apparent specific heat on heating have now been carried out on some aluminium-4% copper and aluminium-4% copper-tin alloys of very high purity. The technique employed

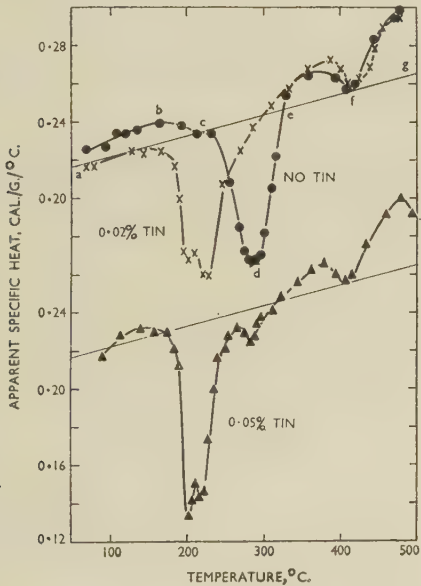


Fig. 1.—Apparent-Specific-Heat/Temperature Curves of Quenched Aluminium-4% Copper-Tin Alloys.

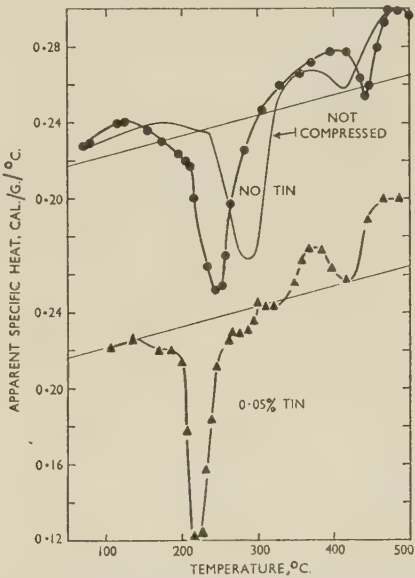


Fig. 2.—Apparent-Specific-Heat/Temperature Curves of Aluminium-4% Copper-Tin Alloys Quenched and Compressed 5%.

temperatures. The rate of artificial ageing was greatly enhanced,¹ whilst metallographic² and X-ray^{3,4} work showed that the ternary elements stimulated the formation of θ' at the expense of the G.P. zones [1] and [2].

differed only in details from that developed by Sykes⁵ and Sykes and Jones⁶ and used by Swindells and Sykes.⁷ The results on alloys which were forged, solution-treated at 530° C., and quenched are given in Fig. 1, whilst Fig. 2 covers specimens which were

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compressed 5% before testing. The rate of heating was 1.4°–2.0° C./min.

The curve for the quenched binary alloy (Fig. 1) was very similar to that obtained by Swindells and Sykes.⁷ The line *acefg* is the calculated specific-heat/temperature curve for a mixture of aluminium with 4% copper in the absence of any phase changes. The specific-heat curve for the alloy lay above the mixture line at temperatures up to 220° C. The area *abc* represents the energy required to re-dissolve the G.P. zones [1] formed at room temperature and immediately above during the heating. The curve for the alloy lay below the mixture line between 220° and 325° C. The area *cde* represents the energy evolved on precipitation of G.P. zones [2] and θ' . Energy absorbed on re-solution raised the alloy curve above the mixture line at temperatures above 325° C. The dip almost back to the mixture line at *f* can be associated with the energy liberated by the transition from θ' to θ .

A considerable difference is effected by the presence of 0.02% tin. The rapid evolution of heat on precipitation began at 185° C. and the maximum rate of heat evolution was at 225° instead of 285° C. in the binary alloy (*d*). The change from θ' to θ took place over a similar temperature range in both the binary and ternary alloys.

The alloy with 0.05% tin showed similar characteristics, but the maximum rate of heat evolution was increased. The minimum apparent specific heat was 0.134 cal./g./°C. at 200° C., compared with 0.168 cal./g./°C. at 285° C. in the binary alloy (*d*). Small fluctuations occurred at 210° C. in the alloys containing tin, and a second small evolution was recorded at 285° C. in the alloy with 0.05% tin.

The heats evolved on precipitation (area *cde*) were 4.03, 4.38, and 4.18 cal./g. for the 0, 0.02, and 0.05%

tin alloys, respectively, and compare well with the values of 4.10–4.40 cal./g. given by Swindells and Sykes for the binary aluminium–4% copper alloy.

The specific-heat curve of the binary alloy was appreciably altered by cold work (Fig. 2). Precipitation started at a lower temperature and the maximum rate of heat evolution was found at 245° C. On the other hand, the temperature for the maximum rate of change of θ' to θ was shifted from 415° to 440° C.

The curve for the ternary alloy was less affected by the same degree of cold work. However, precipitation occurred over a narrower range of temperature, and the minimum apparent specific heat was 0.122 cal./g./°C. at 220° C. A small heat absorption was recorded at 300° C.

The heat evolved on precipitation was 4.11 cal./g. and 4.23 cal./g. for the cold-worked binary and ternary alloys, respectively.

The extremely great acceleration of the precipitation process due to tin, revealed and confirmed by the specific-heat measurements, supports the view that tin (and also indium and cadmium) facilitates the nucleation process. Cold work speeded up precipitation in the binary alloy, but had little effect on the shape of the specific-heat curve for the alloy with 0.05% tin, although the minimum specific-heat value tended to occur at a slightly higher temperature.

REFERENCES

1. H. K. Hardy, *J. Inst. Metals*, 1951–52, **80**, 483.
2. I. J. Polmear and H. K. Hardy, *ibid.*, 1952–53, **81**, 427.
3. J. M. Silcock, T. J. Heal, and H. K. Hardy, *ibid.*, 1953–54, **82**, (6), 239.
4. J. M. Silcock, T. J. Heal, and H. K. Hardy, in preparation.
5. C. Sykes, *Proc. Roy. Soc.*, 1935, [A], **148**, 422.
6. C. Sykes and F. W. Jones, *J. Inst. Metals*, 1936, **59**, 257.
7. N. Swindells and C. Sykes, *Proc. Roy. Soc.*, 1938, [A], **168**, 237.

THE SLIP-BAND EXTRUSION EFFECT OBSERVED IN SOME ALUMINIUM ALLOYS SUBJECTED TO CYCLIC STRESSES *

1611

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SYNOPSIS

Extrusion of crystalline material from slip bands has been observed during the final stages of fatiguing of a number of solution-treated materials. The extruded material is in the form of ribbon, the thickness of which is estimated as less than 0.1μ . It appears suddenly after a period of cyclic stressing and leaves behind a crevice which represents the initial crack. The effect may be associated with a segregation or ordering of the solute atoms in the lattice. This ordering may to a certain extent already exist in the solution-treated material, but it is mainly the result of the action of the cyclic stresses on the metastable matrix.

I.—INTRODUCTION

OBSERVATIONS on pure aluminium and an aluminium- $\frac{1}{2}\%$ silver alloy in earlier fatigue investigations^{1, 2} have consistently revealed a considerable degree of local deformation under the action of cyclic stresses. This deformation occurred as finely spaced slip bands which congregated in the form of striations. The mode of development of the striations has been discussed, and it was concluded that in these materials the striated form was characteristic of the fatigue process.

Aluminium-4% copper alloys, in the metastable solution-treated condition, however, revealed no tendency to form striations under the action of cyclic stress, the very fine slip bands which appeared being fairly uniformly distributed across the grains. After a period of fatiguing, the material cracked along a number of slip planes, producing a cleavage fracture. Some of the grains contained a number of parallel cracks, usually following the operative slip planes but sometimes lying along other planes. These cracks generally exhibited what appeared to be surface debris distributed along their length.¹ A study of the nature and occurrence of this debris forms the subject of the present paper.

The technique of fatiguing employed was the same as in previous work,^{2, 3} i.e. reverse plane bending.

II.—EXPERIMENTAL RESULTS

1. THE EXTRUSION EFFECT AT ROOM AND SUB-ZERO TEMPERATURE

Some of the results of a micrographic examination of aluminium-4% copper specimens are presented in Figs. 1-12 (Plates LX and LXI). Fig. 1 shows a specimen fatigued at room temperature after electro-

polishing. Numerous cracks have formed across the grains, and an irregular distribution of debris is to be observed along the length of the cracks. Fig. 2, at a higher magnification, illustrates the appearance of this debris. It consists of thin ribbons of material standing proud of the metal surface. By means of the marked stereoscopic effect to be obtained at high magnifications by modification of the microscope lighting train, &c., it was possible to get a good idea of the nature of this phenomenon. The extrusion usually occurred discontinuously across the surface, obviously following the trace of some crystal plane. This is particularly noticeable in Fig. 2. Fig. 3 reveals extrusion marks on the ribbon (arrow *A*), presumably produced by irregularities along the plane of extrusion. Although the ribbon was generally extruded along an operative slip plane, extrusion occasionally followed a plane at an angle to this, and one on which no slip had previously been visible. An example is shown in Fig. 4 (arrow *B*). In the case of the aluminium-4% copper alloy, the limit of height of the extruded ribbons seemed to be approximately 10μ ; the length in the plane of the crystal surface varied considerably, some extending almost across the grains and others being only $1-2 \mu$ long. The thickness appeared to be fairly constant, as judged by the curvature of the ribbon that occurred.

No direct microscopical measurements of the thickness could be made, as this was almost certainly less than the resolution of the optical microscope, and since the ribbons always curled at the edges, no edge-on view could be obtained. However, an estimated upper limit of 0.1μ was reached by means of interference-fringe measurements on a specimen surface on to which some of the ribbons had been flattened.

In order to investigate the metallic nature of these ribbons, some were stripped on to a Perspex replica,

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produced by compressing a Perspex block together with Perspex powder against the specimen surface, and hot compacting in a metallographic mounting press. The stripped ribbons were examined with transmitted light and found to be completely opaque, thus confirming the metallic nature suggested by their high reflectivity when seen in the metallographic microscope. In Fig. 5 the stripped ribbons may be seen lying on the Perspex replica, as viewed with vertical illumination.

The appearance of the debris on the surface coincided with a change in the natural frequency of the specimen during the fatigue test, and was followed by rapid failure. It was therefore suspected that the extrusion of ribbon from the surface left a crevice which could not heal. To confirm that a loss of cohesion had occurred, specimens were repolished and pulled in order to open out any incipient cracks. Elliptical cracks were formed along all the regions from which extrusion had taken place. Even so, it was evident from the plastic deformation that occurred at the ends of the cracks that the surface material was still ductile to a slowly applied tensile stress. Figs. 6 and 7 show grains after fatigue, extrusion, and subsequent tension.

If a region of slip-band extrusion was repolished and heavily etched in 10% NaOH solution, the crevices left by the extrusion deepened and widened (Fig. 8, arrow *A*), and the reagent also produced furrows across the crystal surface in the direction in which extrusion had occurred. These furrows seemed to be traces of planes on which some change preceding extrusion had been taking place. Their appearance suggested that the chemical behaviour of the crystal differed along these planes. This might be the result of plastic deformation, or possibly of some rearrangement or segregation of the solute atoms. Fig. 8 shows a group of such regions.

The fact that the extrusion phenomenon occurred in aluminium-4% copper alloy, which has marked age-hardening properties, suggested that it might be associated with the ageing effect. It has been established by Hanstock⁴ that vibration accelerates the precipitation process in commercial light alloys of the age-hardening type.

Accordingly, a number of low-temperature fatigue tests were carried out to check the influence of ageing on the extrusion effect. Ageing, being a diffusion process, is highly temperature-dependent, and, as had been expected, when the aluminium-4% copper alloy was fatigued at -25°C . the extrusion effect was greatly reduced and the material behaved in a completely different manner. Instead of the sharply defined slip-band extrusion and straight cracks, the crystals deformed under the action of the cyclic stresses in a manner similar to that of pure aluminium, i.e. a number of striations were formed across the crystals. The slip bands constituting these striations must have been very fine, as it was not possible to resolve them. At lower temperatures, down to -90°C ., the extrusion effect was almost com-

pletely suppressed. Fig. 9 shows striations produced by fatiguing under liquid nitrogen, and Fig. 10 a striation after repolishing, where an irregular crack has started. On subsequent elevated-temperature ageing of specimens fatigued at these low temperatures, more marked precipitation occurred in these striations, delineating the boundaries of small crystallites, which seemed to have been produced during the fatigue process (Fig. 11). The cracks appeared to follow regions denuded of copper, as shown by the density of the subsequently formed precipitate (Fig. 12). This indirect method of ascertaining the state of the matrix after the cyclic stressing is, unfortunately, open to question, as both the polygonization (Fig. 11) and the appearance of the denuded zones surrounding the cracks in Fig. 12 may have been due to the ageing temperature.

2. EFFECT OF DEGREE OF SUPERSATURATION

All the observations recorded above were made on the aluminium-4% copper alloy in the solution-treated and quenched condition, i.e. in the highest possible state of supersaturation. If the extrusion process is associated with ageing, this condition should give rise to the greatest amount of slip-band extrusion. To check this, the alloy was fatigued in the following conditions:

- (i) Solution-treated, quenched, and aged at 150°C . for 66 hr.
- (ii) Solution-treated, quenched, and aged at 350°C . for 16 hr.
- (iii) Furnace-cooled from 520°C .

Extrusion was in every case greatly reduced or completely eliminated. Condition (i), which is near the peak of the hardness/time curve for the alloy aged at that particular temperature, produced a very small amount of ragged extrusion. In condition (ii) no extrusion occurred, the slip bands formed being widespread and situated in short lengths between the visible precipitate. Condition (iii) led to a small amount of extrusion, similar in nature to but far less profuse than that found in the solution-treated and quenched material.

From these observations it would seem that if an alloy were metastable at a test temperature at which ageing could take place in a reasonably short time, then extrusion should occur. On the other hand, in a solid solution stable at room temperature it should be absent. The solubility of copper in aluminium at room temperature is very low, and the possibility that a few scattered regions of segregation might arise in such an alloy would interfere with the observations. It was therefore decided to use a series of aluminium-zinc alloys. The room-temperature solubility of zinc in aluminium⁵ is given as 2%, rising with increase in temperature to 100°C . to approximately 5%. The three alloys chosen accordingly contained, respectively, 2, 5, and 10% zinc.

A specimen of the aluminium-2% zinc alloy was

solution-treated at 200° C. for 2 hr., then electro-polished and fatigued. The alloy deformed in a manner very similar to that of pure aluminium and no extrusion was observed. Extrusion was also absent from the 5% zinc alloy, but was found in the aluminium-10% zinc alloy, which also suffered from grain-boundary cracking at room temperature. At sub-zero temperatures this alloy showed more slip-band extrusion than at room temperature, but no boundary cracking. An example of the extrusion is given in Fig. 13 (Plate LXI). At low temperatures extrusion often occurred in "blocks" in this particular alloy. On testing down to -195° C. extrusion was still prevalent, though a few small striations were found.

3. LOW-FREQUENCY TESTS

A number of earlier observations had suggested that the temperature in the region of active slip planes subjected to cyclic stresses might rise considerably and that the temperature gradient and maximum temperature attained in these regions would depend on the frequency. It was therefore considered that the frequency of the test might influence the slip-band extrusion phenomenon, if it were associated with ageing on slip planes due to a local rise in temperature. There was, however, no difference in appearance between the extrusion formed at 100 cycles/sec. and that formed at 1 cycle/sec. It was found that the extrusion occurred suddenly, within a few cycles, after a period of fatiguing.

4. EXTRUSION ON PLANES RUNNING OBLIQUELY TO THE SURFACE

During the fatiguing of aluminium-4% copper alloy, it was noticed that corrugations sometimes appeared in the metal surface adjacent to the edges of cracks from which extrusion had occurred. It was found that in these particular grains the active planes were obliquely orientated to the surface; thus a thin "chisel edge" of material was left unsupported after extrusion, and loss of cohesion occurred. The corrugated nature of this edge suggested that a certain amount of internal stress had been relieved by the cracking. This is discussed more fully in Section III. Fatigue tests were made on very thin material (approximately 0.005 in. thick), in which most of the grains could be identified on both sides of the specimen. Occasionally a grain was found that showed corrugations along the edges of the slip-band extrusion regions. The same grain on the reverse face of the specimen exhibited an identical extrusion effect and a similar corrugated nature, again associated with the chisel edge of the material. It was also possible to identify active planes, to confirm that extrusion had occurred from each end, and to estimate the angle the active plane made with the surface and hence the angle of the chisel edge. The height of the surface rumpling was measured interferometrically and found

to be approximately 0.2 μ . The superficial dimensions of these regions were of the order of 10 μ . Very fine slip bands were observed in these rumpled regions running parallel to the crack, and another set of bands at an angle to the crack. From this it was deduced that the rumpling was not due merely to the relief of internal elastic stress, but that plastic deformation had been caused in these regions by a form of stress concentration.

5. EFFECT OF SOLUTION-TREATMENT TEMPERATURE

It was found that the solution-treatment temperature might influence the subsequent deformation and appearance of the slip-band extrusion. In the case of the aluminium-4% copper alloy, the α range is not great, and only a slight difference in behaviour was observed in specimens solution-treated at extremes of the range; but with an aluminium-8% silver alloy, specimens solution-treated at 400° C. and subsequently quenched produced slip-band extrusion (Fig. 15, Plate LXI), whereas material solution-treated at 550° C. exhibited only striations and an intermediate type of extrusion resembling a fold in a piece of cloth. The extrusion effect could be restored by a rapid ageing (200° C. for 5 min.) before fatiguing (Fig. 16, Plate LXI). These observations suggest that, in this alloy at least, slip-band extrusion did not occur in a completely random solid solution, but only in one which was to some extent ordered.

6. OTHER ALLOY SYSTEMS

A few observations were made on alloy systems other than those already described, in particular to determine whether various age-hardening systems could produce slip-band extrusion. In general, some form of slip-band extrusion occurred in all the alloys examined.

III.—DISCUSSION

The formation of crystal debris, as the direct consequence of attrition of the crystal planes when subjected to cyclic movements, had been suggested, or at least implied, by Ewing and Humfrey⁶ in their early "attrition" theory of fatigue. In the previous work on pure aluminium and aluminium- $\frac{1}{2}$ % silver alloys,^{1,2} no evidence of debris had been encountered, the roughened appearance of the slip bands having been shown to be due to glide on closely spaced lamellæ, producing minute ridges and grooves which could be observed interferometrically. No sign of extrusion from slip planes was found with annealed pure aluminium, but on the other hand slip striations or packets of visible slip bands were often pushed up above the general level of the surface, as in fact Ewing and Humfrey had also observed. The height of these striations was very small, compared with the distance that the true extrusion covers. Evidence now appears to be forthcoming of a gradual transition from the

rising of wide striations to the more marked eruption of narrower, sharply defined striations, and then to the extreme case of extrusion of definite ribbons.

In all these effects, where a region of material is erupting, either as a thick striation or as a very thin ribbon, it seems reasonable to assume that the region is softer than the surrounding crystal and that deformation is therefore concentrated within it. It is therefore also reasonable to suppose that the narrower the region, the more concentrated is the movement and the greater the distance of extrusion, irrespective of the nature of the extrusion mechanism. Striations and extrusions may therefore be considered as resulting from the same general cause, i.e. a concentration of deformation due to the existence of soft regions. The difference in width between the striations in the pure metal and the extrusion bands in the alloys is probably due to some concentrating factor in the alloys, such as an overageing effect, i.e. re-arrangement of the solute atoms resulting in a soft region in the crystal. The processes whereby soft spots are produced and continue to deform under cyclic stresses would seem to constitute the fundamental origins of fatigue.

The two extreme types of deformation and failure, though possibly both arising from the formation of soft regions in the crystal, are quite distinct in their development. In the first type, of which the aluminium-4% copper alloy is an example, certain slip bands extrude, leaving behind a crevice. Even in these alloys, however, not all the cracks exhibit extrusion and not all the extrusion and cracking is confined to the operative slip planes (Fig. 4, Plate LX); it sometimes occurs on planes making a small angle with the operative slip planes. In the second type, found in stable materials, such as pure aluminium and aluminium-4% copper alloys at temperatures low enough to suppress ageing, striations of slip bands form in which short, irregular cracks appear. The fact that the aluminium-4% copper alloy will revert to the formation of striations and eventual cracking in the manner of pure aluminium when fatigued at low temperatures, at which the ageing rate is very slow, suggests that the ageing process is intimately connected with the extrusion effect.

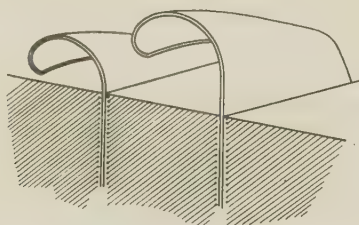


FIG. 17.—Schematic Diagram of Slip-Band Extrusion.

The mechanism of slip-band extrusion has been closely studied by means of the stereo-optical microscope at high magnifications, and its geometrical form appears to be as shown in Fig. 17. This is typical of most of the material produced, but Fig. 18 illustrates schematically the different types of extrusion observed,

including the block formation sometimes seen in the aluminium-10% zinc alloy. The anvil type of extrusion, illustrated photographically in Fig. 2 (Plate LX) and diagrammatically in Fig. 18 (b), presumably

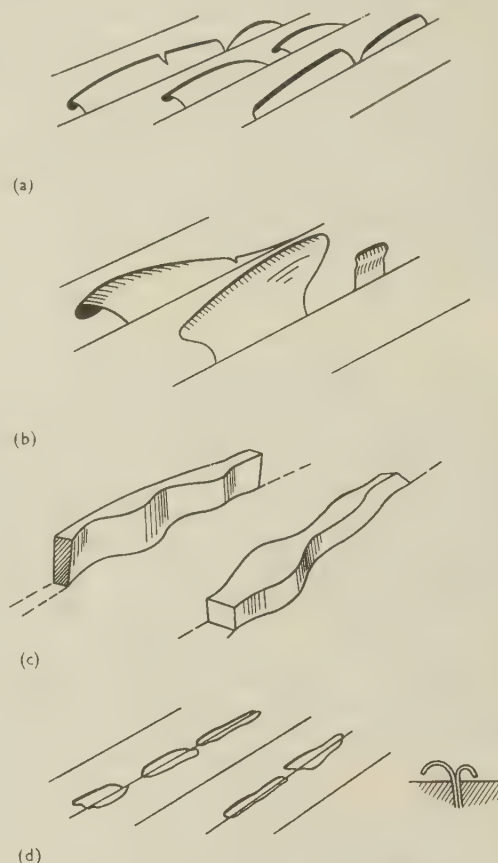


FIG. 18.—Types of Slip-Band Extrusion.

- (a) General extrusion (e.g. Al-4% Cu alloy at room temperature).
- (b) Anvil type (e.g. Al-4% Cu alloy at room temperature).
- (c) Block extrusion (e.g. Al-10% Zn alloy at $-60^{\circ}\text{C}.$).
- (d) Double slip-band extrusion (e.g. Al-5% Mg alloy at room temperature).

occurs when the extrusion direction lying in the extrusion plane is at some angle other than normal to the slip band. The irregularities in extrusion rate show themselves as kinks and cracks in the extruded ribbon, and no doubt account for its crinkled nature. This crinkled or kinked appearance, particularly the marks shown on the large extrusion in Fig. 2 (Plate LX), give the impression that the ribbon is extremely thin, even compared with its superficial dimensions. The corrugated nature of the chisel edge sometimes found along the crack, and illustrated in Fig. 14 (Plate LXI), affords evidence for localized internal stresses and no doubt these play a part in the irregular extrusion rate and crinkling. Such an edge is schematically drawn in Fig. 19. The dimensions shown are typical and were observed on an aluminium-4% copper specimen. The deformed region is geometrically complex and no useful determinations of internal stress could be made, but it is significant that

small subsidiary slip bands are present, indicative of plastic deformation.

Any description of the atomic events leading up to slip-band extrusion must at this stage be only conjecture. The data required to establish the mechanism by which these regions are first formed include: (i) the chemical composition of the extruded ribbon; and (ii) evidence for or against segregation of solute atoms in the extruded regions. If these data suggest

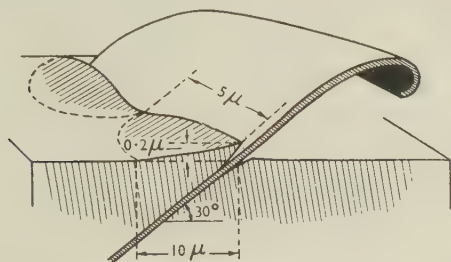


FIG. 19.—Schematic Diagram Showing the Distortion of the Crystal Sometimes Observed when Extrusion Occurs. The dimensions shown are typical and approximate.

that soft spots are produced, then the extrusion may be considered as a logical consequence. Whether the effect is one of direct extrusion or of a gliding movement along the slip plane depends on the mechanical properties of the ribbon, but it would seem highly improbable that a true extrusion effect due to pressure normal to the extrusion plane, can readily occur. Further work now in progress is directed towards determining whether segregation of solute atoms is induced by the application of fatigue stresses, and to correlating the extrusion phenomenon with the cracking observed in commercial light alloys.

IV.—CONCLUSIONS

(1) Solution-treated aluminium-4% copper alloy, when subjected to fatigue stresses, fails by cracking along certain sharply defined planes, usually operative slip planes.

(2) The occurrence of these cracks seems to be coincident with the formation and extrusion of metallic ribbon. This phenomenon has been named slip-band extrusion. The extruded ribbons leave crevices in the crystal surface which often develop into the initial fatigue cracks, although cracks sometimes develop also without the formation of ribbon. The slip-band extrusions described here are less than 0.1μ thick and often exhibit extrusion marks.

(3) The extrusion effect and formation of the

crevice seem to release a certain amount of internal stress, resulting in an undulating edge to some of the fatigue cracks. Subsequent static stress opens out the cracks, the material at the ends still showing marked ductility.

(4) Occasionally extrusion is found to occur along planes making a small angle with the operative slip planes, and sometimes where no previous slip has been visible.

(5) Tests at low frequencies (1 cycle/sec.) showed no difference in the slip-band extrusion effect from those at the normal frequency (100 cycles/sec.), and it is therefore considered that any temperature rise associated with the extrusion process is very local. At this low frequency it was possible to observe that the extrusion appears suddenly, within a period of a few cycles.

(6) At liquid-nitrogen temperature the slip-band extrusion effect in aluminium-4% copper alloys is suppressed and striations are formed similar to those produced in pure aluminium.

(7) 10% NaOH solution etches furrows along what seem to be planes of incipient slip-band extrusion where apparently some change prior to extrusion has taken place. This observation, coupled with the fact that the slip-band extrusion effect can be suppressed in the aluminium-4% copper alloy by reducing the test temperature, suggests that it is associated with accelerated ageing under the action of cyclic stresses.

(8) It is concluded from the occasional absence of slip-band extrusion from some cracks, that the effect is not itself a necessary part of the fatigue-cracking process, but is only a by-product of the type of brittle fracture that characterizes these unstable alloys. Its importance lies in the fact that it provides a clue to the nature of the change that occurs on certain planes under the action of fatigue stresses.

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REFERENCES

1. P. J. E. Forsyth, *Nature*, 1953, **171**, 172.
2. P. J. E. Forsyth, *J. Inst. Metals*, 1951-52, **80**, 181.
3. P. J. E. Forsyth, *ibid.*, 1953-54, **82**, (9), 449.
4. R. F. Hanstock, *ibid.*, 1948, **74**, 469.
5. L. F. Mondolfo, "Metallography of Aluminium Alloys". 1943: New York (John Wiley and Sons, Inc.).
6. J. A. Ewing and J. W. C. Humfrey, *Phil. Trans. Roy. Soc.*, 1903, [A], **200**, 241.

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3. **Manuscripts and illustrations** should be submitted in duplicate. MSS. must be typewritten (*double-line spacing*) on one side of the paper only, and authors are requested to sign a declaration that neither the paper nor a substantial part thereof has been published elsewhere. Exceptions may be made in certain cases where a paper has been published in a language other than English, French, German, or Italian (see 2(d) above). MSS. not accepted are normally returned within 6 months of receipt.

In the interests of economy, all papers must be written as concisely as possible; in general, internal research reports are not in suitable form for publication as papers in the *Journal*. All but the simplest mathematical expressions should be written by hand, with capital and small letters clearly distinguished. Superscript and subscript letters should also be plainly indicated. Greek letters and special signs should be identified in the margin. For style, spelling, and abbreviations used, any recent issue of the *Journal* may be consulted.

4. **Synopsis.** Every paper must have a synopsis (not exceeding 250 words in length) which, in the case of a paper reporting original research, should state its objects, the ground covered, and the nature of the results. The synopsis will appear at the beginning of the paper, and should be in a form suitable for use by abstracting organizations. Extracts from a "Guide for the Preparation of Synopses" drawn up by the Abstracting Services Consultative Committee are reproduced below.

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A. L. Dighton and H. A. Miley, *Trans. Electrochem. Soc.*, 1942, 81, 321 (i.e. year, volume, page).

References to books should be in the following style:

C. Zener, "Elasticity and Anelasticity of Metals". 1948: Chicago (University of Chicago Press).

6. **Illustrations.** Each illustration must have a number and description; only one set of numbers must be used in one paper, and it is desirable to number the half-tone illustrations consecutively, rather than to intersperse them with the line figures. The captions should be typed on a separate sheet.

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GUIDE FOR THE PREPARATION OF SYNOPSSES

(As recommended by the Abstracting Services Consultative Committee)

1. **Purpose.** The synopsis is not part of the paper; it is intended to convey briefly the content of the paper, to draw attention to all new information, and to the main conclusions. It should be factual.

2. **Style of writing.** The synopsis should be written concisely and in normal rather than abbreviated English. It is preferable to use the third person. Where possible use standard rather than proprietary terms, and avoid unnecessary contracting.

It should be presumed that the reader has some knowledge of the subject, but has not read the paper. The synopsis should therefore be intelligible in itself without reference to the paper; for example, it should not cite sections or illustrations by their numerical references in the text.

3. **Content.** The title of the paper is usually read as part of the synopsis. The opening sentence should be framed accordingly and repetition of the title avoided. If the title is insufficiently comprehensive, the opening should indicate the subjects covered. Usually the beginning of a synopsis should state the objective of the investigation.

It is sometimes valuable to indicate the treatment of the subject by such words as: brief, exhaustive, theoretical, &c.

The synopsis should indicate newly observed facts, conclusions of an

experiment or argument and, if possible, the essential parts of any new theory, treatment, apparatus, technique, &c.

It should contain the names of any new compound, mineral species, &c., and any new numerical data, such as physical constants; if this is not possible, it should draw attention to them. It is important to refer to new items and observations, even though some are incidental to the main purpose of the paper; such information may otherwise be hidden, though it is often very useful.

When giving experimental results the synopsis should indicate the methods used; for new methods the basic principle, range of operation, and degree of accuracy should be given.

4. **References.** If it is necessary to refer to earlier work in the summary, the reference should always be given in full and not by number. Otherwise references should be left out.

When a synopsis is completed, the author is urged to revise it carefully, removing redundant words, clarifying obscurities, and rectifying errors in copying from the paper. Particular attention should be paid by him to scientific and proper names, numerical data, and chemical and mathematical formulae.



FIG. 4.—As-Cast 1% Aluminium β -Brass (NHH), Showing "Clean" Boundaries. $\times 2000$.



FIG. 5.—As-Cast 3% Aluminium β -Brass (NSG), Showing Grain-Boundary Pitting. $\times 1500$.



FIG. 6.—As-Cast Super-Pure 4% Aluminium β -Brass (NGP), Showing Grain-Boundary Pitting. $\times 2000$.



FIG. 7.—As-Cast 5% Aluminium $\beta + \gamma$ -Brass (NCC), Showing Fine and Coarse Pitting. Also shows massive γ in grain boundary on left. $\times 2000$.



FIG. 8.—As-Cast 4% Aluminium β -Brass (NGP) Quenched in Water from 800° C., Showing Grain-Boundary Pitting. $\times 1500$.



FIG. 9.—Grain-Boundary Pitting in 1% Aluminium β -Brass (NHH) Coated with Aluminium and Annealed at 600° C. for 3 Days. $\times 2000$.

All photographs are of electropolished specimens unless otherwise stated.

[To face p. 400.

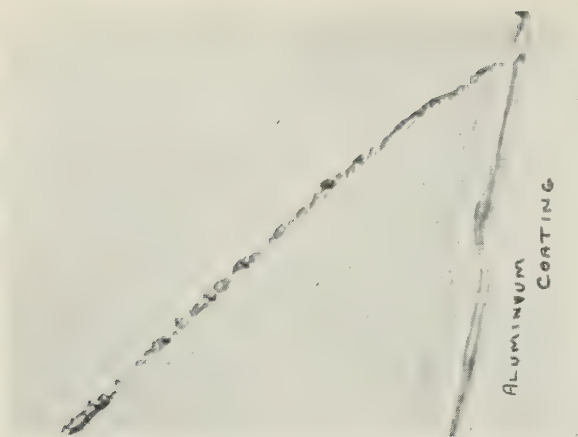


FIG. 10.— γ Particles in 4% Aluminium β -Brass (NGP) Coated with Aluminium and Annealed at 600° C. for 2 Days. $\times 1500$.

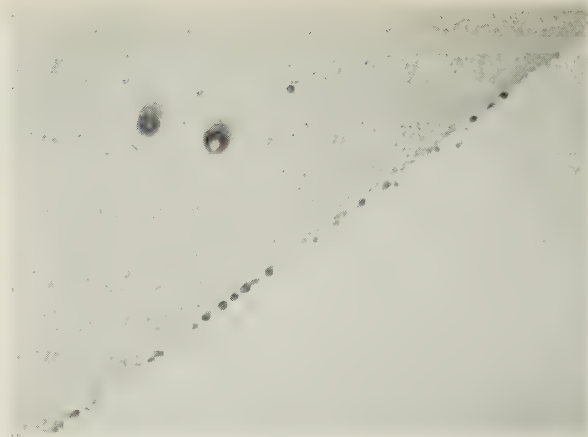


FIG. 11.—Same Boundary as in Fig. 10, but Further Away from the Aluminium Coating, Showing Pitting. $\times 1500$.



FIG. 12.—5% Aluminium α -Brass (NYH) Cold-Worked and Recrystallized. $\times 300$.



FIG. 13.—As-Cast 5% Aluminium Brass (NCC). Shows grain-boundary pitting corresponding to fine pitting in Fig. 7. $\times 10,000$.



FIG. 14.—As-Cast 5% Aluminium Brass (NCC). Grain boundary which showed coarse pitting under the light microscope, see Fig. 7. $\times 10,000$.

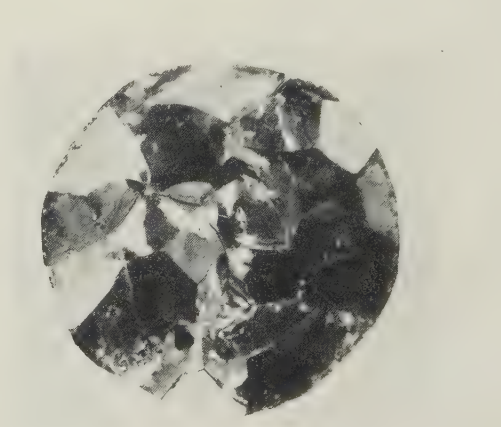


FIG. 15.—Typical Intercrystalline Fracture of a β -Brass Impact Tensile Specimen Tested at 400° C. $\times 6$.

All photographs are of electropolished specimens unless otherwise stated.

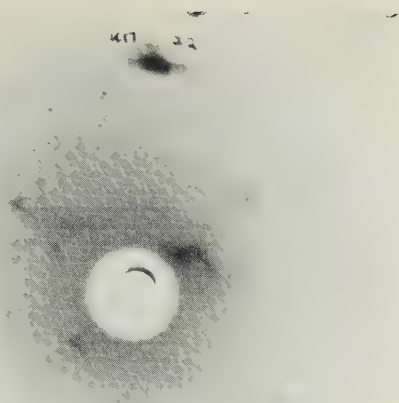


FIG. 16.—Back-Reflection Laue Photograph from a Facet of an Inter-crystalline Fracture in the 3% Aluminium β -Brass (NSG).

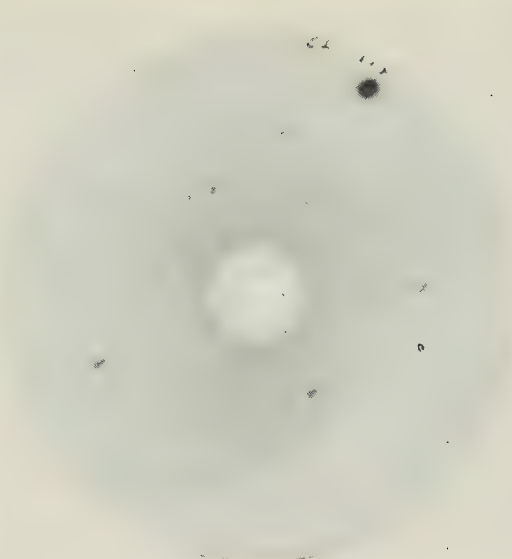


FIG. 17.—Same as Fig. 16 After Etching the Facet for a Short Time in 50% Nitric Acid.



FIG. 18.—Taken from a Facet Perpendicular to the Stress in Specimen Fractured at 500° C.



FIG. 19.—Taken from a Facet Almost Perpendicular to the Stress in Specimen Fractured at 500° C.

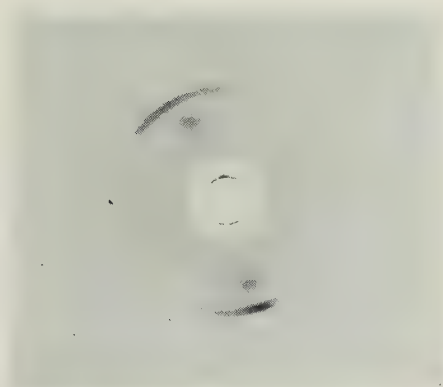


FIG. 20.—Taken from Facet at 60° to Direction of Stress in Specimen Fractured at 400° C.

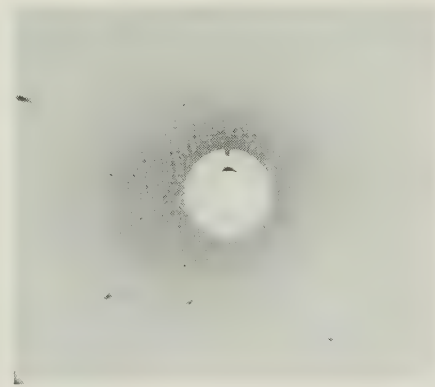


FIG. 21.—Same as Fig. 20 After Removing a Thickness of 16 μ by Electropolishing.

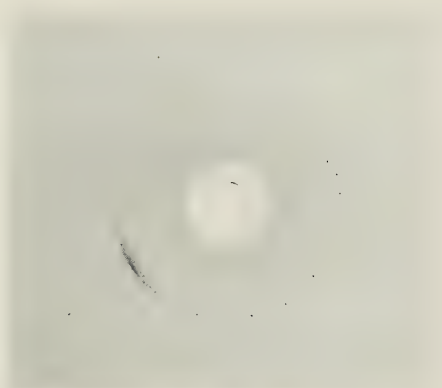


FIG. 22.—Taken from Facet at 30° to Direction of Stress in Specimen Fractured at 400° C.

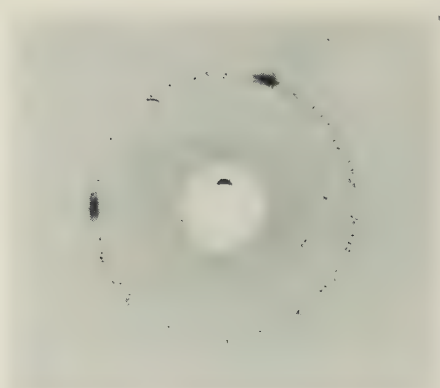


FIG. 23.—Taken from Facet Parallel to Direction of Stress in Specimen Fractured at 400° C.

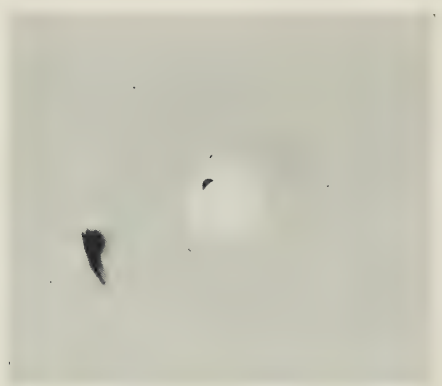


FIG. 24.—Same as Fig. 23 After Removing a Thickness of 100 μ by Electropolishing.

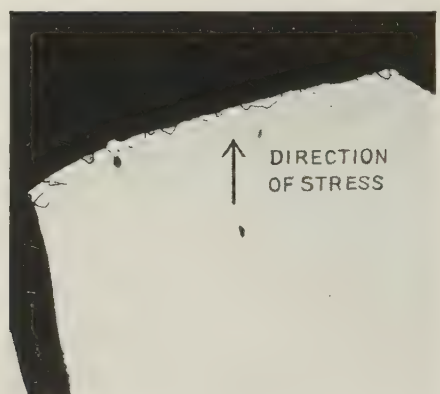


FIG. 25.—Extruded Plain β -Brass Fractured at 400° C. $\times 250$.

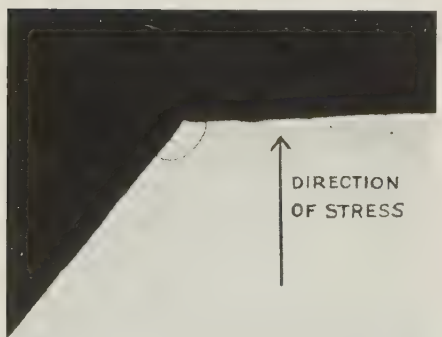


FIG. 26.—As-Cast β -Brass Containing 3% Aluminium Fractured at 500° C. $\times 200$.

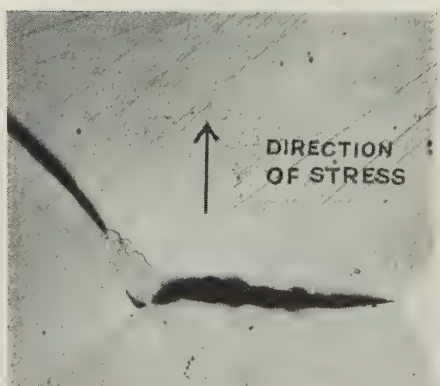


FIG. 27.—Same Specimen as Fig. 25. $\times 200$.

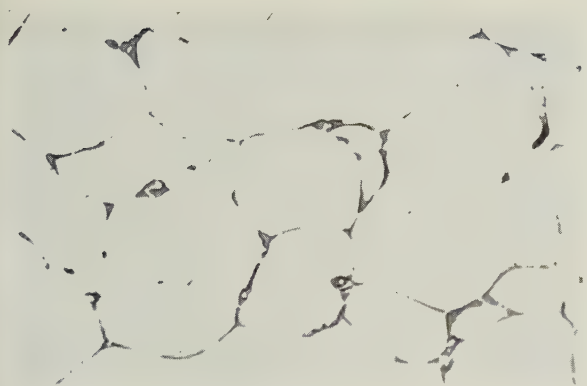


FIG. 1.—4% Aluminium β -Brass Containing 0.35% Zirconium.
Sand cast. Etched in 20% HF + 1% HNO₃. $\times 250$.



FIG. 2.—4% Aluminium β -Brass Containing 0.06% Zirconium.
Chill cast. Etched in 10% ammonium persulphate. $\times 400$.



FIG. 3.—4% Aluminium β -Brass Containing 0.06% Titanium.
Chill cast. Etched in 10% ammonium persulphate. $\times 1000$.

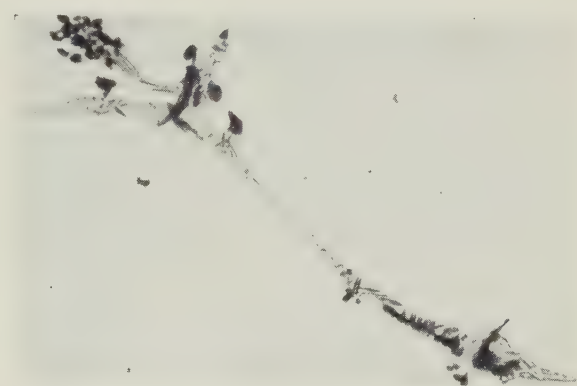


FIG. 4.—5% Aluminium β -Brass Containing 0.2% Zirconium.
Sand cast. Etched in 20% HF + 1% HNO₃. $\times 600$.

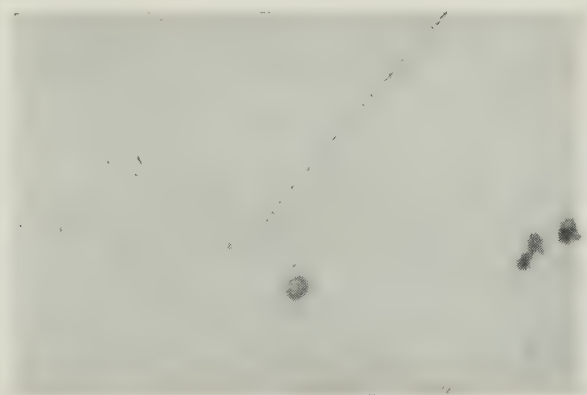


FIG. 5.—0.1% Aluminium β -Brass Containing 0.05% Zirconium.
Quenched from 800° C. Electropolished. $\times 1000$.

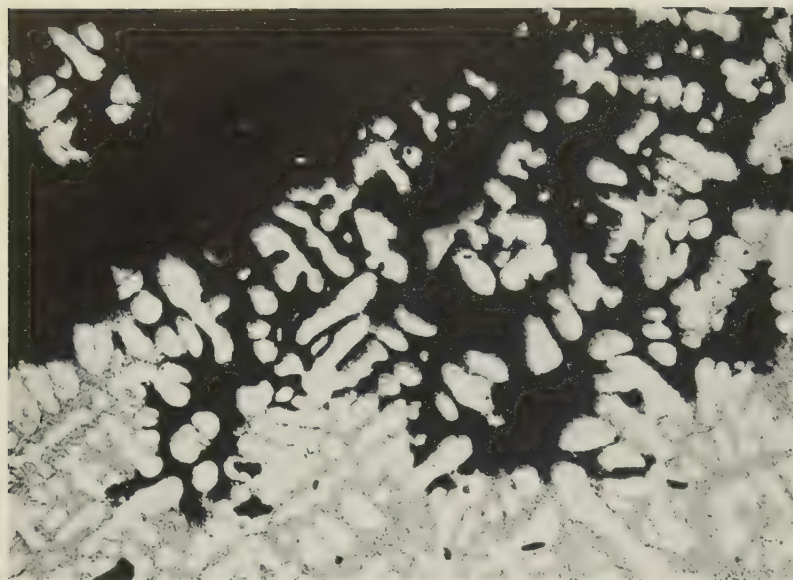


FIG. 1.—Selective Structural Corrosion of a Polyphase Cast Aluminium Alloy. (B.S. 1490 LM9 P.) Unetched. $\times 100$.

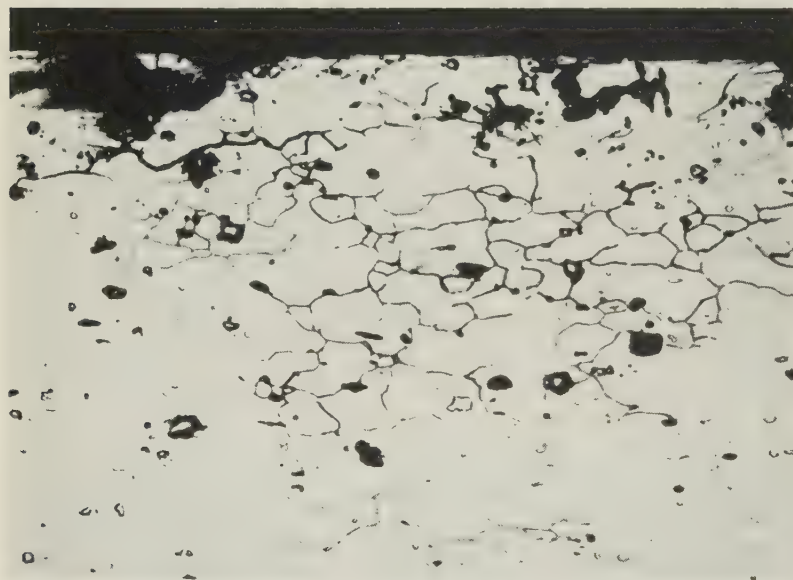


FIG. 2.—Intercrystalline Corrosion of Rolled Aluminium Alloy. HS14 T, inadequately quenched. Lightly etched. $\times 100$.



FIG. 3.—Stress-Corrosion Fracture in Aluminium Alloy under a Tensile Load Equivalent to 75% of Proof Stress. NS7 abnormally aged. Unetched. $\times 26$.

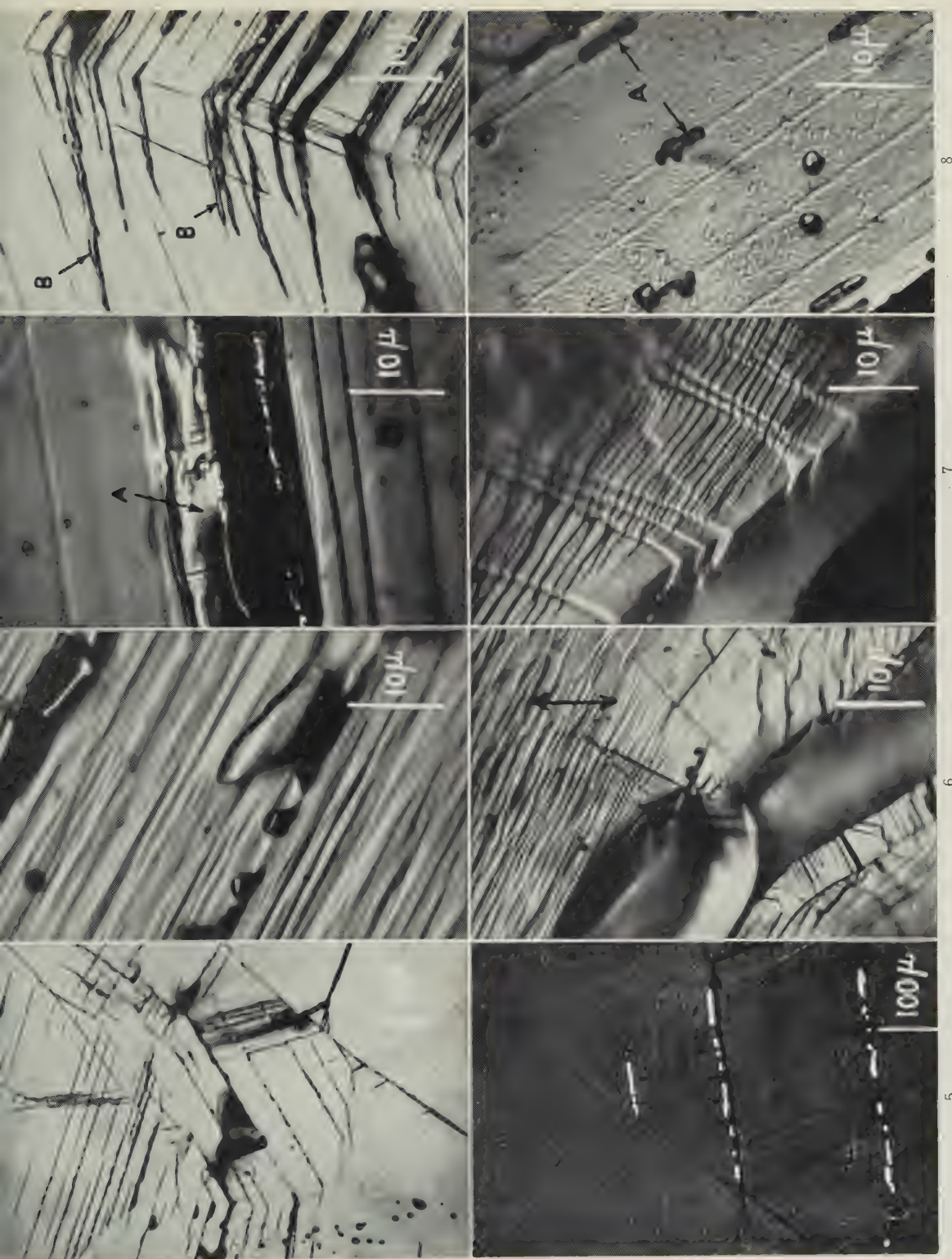


FIG. 1.—Specimen Fatigued at Room Temperature After Electropolishing. $\times 200$.
 FIG. 2.—Anvil-Type Extrusion. $\times 1500$.
 FIG. 3.—Extrusion Marks (indicated by arrow). $\times 1500$.
 FIG. 4.—Extrusion (indicated by arrows) from Planes Other Than the Operative Slip Plane. $\times 1500$.
 FIG. 5.—Perspex Replica with Extruded Ribbon Attached. $\times 100$.

FIG. 6.—Cracks, from Which Extrusion Has Occurred, Opened by Subsequent Tensile Stress Applied as Indicated. $\times 1500$.
 FIG. 7.—Slip Bands Produced at the Edge of a Fatigue Crack by Subsequent Tensile Stress. $\times 1500$.
 FIG. 8.—Region of Slip-Band Extrusion, Repolished and Etched in 10% NaOH. (Arrows show enlarged crevices.) $\times 1500$.

SLIP-BAND EXTRUSION IN ALUMINIUM ALLOYS.

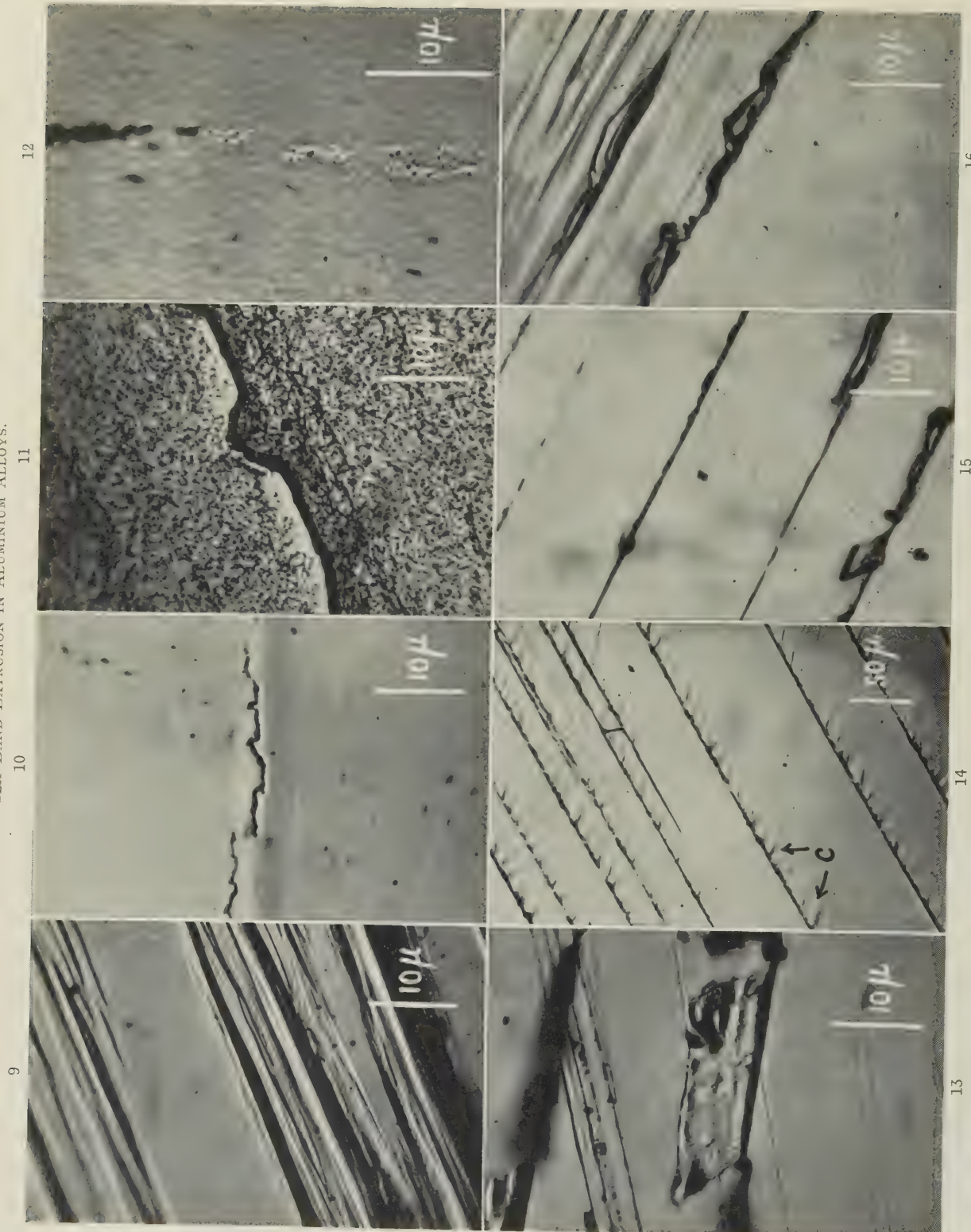


FIG. 9.—Al-4% Cu Alloy Fatigued Under Liquid Nitrogen. $\times 1500$.
 FIG. 10.—Fatigue Cracks in Al-4% Cu Alloy Fatigued at -50°C . (Repolished).
 FIG. 11.—Al-4% Cu Alloy Fatigued at 250°C . $\times 1500$.
 FIG. 12.—Al-4% Cu Alloy Fatigued at 250°C . (Repolished).
 FIG. 13.—Al-10% Zn Alloy Fatigued at -40°C . $\times 1500$.
 FIG. 14.—Al-4% Cu Alloy Fatigued at 1500°C .
 FIG. 15.—Al-8% Zn Alloy Fatigued at 1500°C .
 FIG. 16.—Al-8% Zn Alloy Fatigued at 1500°C .

INHOMOGENEOUS DEFORMATION IN ROLLING AND WIRE-DRAWING *

1612

By B. B. HUNDY,† B.Sc., Ph.D., A.I.M., MEMBER, and A. R. E. SINGER,‡ B.Sc., Ph.D., MEMBER

SYNOPSIS

Microhardness measurements made on copper, 70 : 30 brass, aluminium, and mild steel indicate that there is an analogy between the inhomogeneity of deformation in rolled strip and that in drawn wire. Copper, brass, and aluminium all show surface-hardening when lightly rolled or drawn. The inhomogeneity is dependent on the working conditions, and disappears after moderate reductions by rolling or drawing. The surface-hardening is caused by frictional forces acting between the rolls or die and the metal, and increases as the coefficient of friction increases. In general, a specific surface hardness can be associated with definite frictional conditions.

Rolling and drawing also give rise to a secondary zone of hardening situated between the core and the surface of the metal. This can be observed in both copper and steel, and it does not decrease in magnitude as the reduction is increased. It is believed that secondary hardening is associated with the manner of deformation during rolling and drawing, and is largely independent of friction.

I.—INTRODUCTION

WHEN a metal is plastically strained in tension, it is found to be uniformly worked, that is, the deformation is homogeneous. Many metal-working processes, however, such as extrusion, give a product which is much more heavily deformed in some parts than others, and it is possible that even a slight inhomogeneity may affect the properties and the behaviour in service of wrought metals. Linicus and Sachs¹ have found, for example, that the tensile strength of drawn brass wire is increased by an increase in the angle of the drawing die; this improvement in properties is believed to be due to a greater inhomogeneity of deformation in wire drawn through the higher-angle dies. Inhomogeneity of deformation can also have deleterious effects. A number of workers²⁻⁵ have shown that plastic working can leave residual stresses in a metal, which might easily be the result of inhomogeneous deformation. These stresses are believed to be responsible for such defects as fire-cracking, season-cracking, edge-cracking, alligator-cracking, &c., and should accordingly be kept as low as possible.

Previous workers have used a variety of methods to reveal inhomogeneous deformation. Perhaps the most popular method⁶⁻⁹ has been to study the distortion of a network of fine lines scribed on the material undergoing working. If these lines became curved, inhomogeneous deformation was inferred. As a method of measuring inhomogeneity, however, this procedure is not entirely satisfactory, as, in addition to other objections, it is not easy to analyse the distorted networks, and effects near to the surface of the specimen cannot be determined accurately.

Other investigators^{1, 10, 11} have used the tensile test to show the inhomogeneity of deformation in drawn brass and copper. Their results are in fair agreement, and the main conclusion seems to be that the surface layers of the wire are worked to a greater extent than the rest. Harris¹¹ also showed that, for heavy reductions, the greatest strength occurred midway between the surface and the core of the wire. Similar conclusions have been reached by workers using hardness measurements^{10, 12} and a differential recrystallization technique.¹³

Most of this work was concerned with soft non-ferrous alloys, and there seems to be little information on inhomogeneity in the harder metals. What information there is suggests that the phenomenon of inhomogeneous deformation is not confined to soft metals. Sachs¹⁴ showed that mild steel was strengthened more by drawing through large-angle dies than through low-angle dies, and other workers^{15, 16} found the hardness of drawn steel wire to be greater at the core than in the skin.

Previous work thus shows that these metal-working processes do give an inhomogeneously deformed product, but there is a lack of quantitative data relating the degree of inhomogeneity to the conditions of working. It is the purpose of the work reported here to supply some of these data.

It was thought that the most reliable method of measuring the inhomogeneity of deformation in a wrought material would be by determining the variation in hardness through its thickness. It was believed that this technique would give more accurate and rapid results, capable of quantitative interpretation, than any other method of approach such as X-ray

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diffraction or recrystallization. As it was necessary to measure variations of hardness over small areas, a microhardness tester was used throughout.

The method adopted was to work a uniform sample under controlled conditions. This was then cut and mounted so that a section through its thickness could be polished and examined. Hardness traverses were made across the section, and the variation in hardness through the sample was plotted to give an inhomogeneity curve for each test. Copper was used for the greater part of the experimental work, but some tests were also made on brass, aluminium, and low-carbon steel.

II.—EXPERIMENTAL PROCEDURE

1. MATERIALS AND PROCESSING

Table I summarizes the initial processing of the materials. Usually the strip was 0.2 in. thick and 2 in. wide, and the wire was 20 S.W.G. Tests carried out after the processing described in Table I showed

TABLE I.—*Processing History of the Materials Before Cold Working.*

	Material	Processing History	Annealing Conditions
Strip	O.F.H.C. Copper	Hot-rolled from ingot to 1 in. thick, then cold-rolled to 0.2 in. thick with intermediate anneals after each 25% reduction.	500° C. for 30 min.
	70 : 30 Brass	Hot-rolled from ingot to 0.5 in. thick, then cold-rolled to 0.2 in. thick, with intermediate anneals after each 25% reduction.	620° C. for 30 min.
	Commercial-purity Aluminium	Cold-rolled from ingot to 0.2 in. thick, with intermediate anneals after each 25% reduction.	350° C. for 30 min.
	Mild Steel (0.1% C)	Hot-rolled from ingot to 0.5 in. thick, then cold-rolled to 0.2 in. thick, with intermediate anneals after each 33% reduction.	700° C. for 10 min.
Wire	O.F.H.C. Copper	Obtained from a commercial source in the half-hard condition.	500° C. for 30 min.
	Mild Steel (0.09% C)	Obtained from a commercial source in the normalized condition.	None

that there were no significant hardness variations through the thickness of the test specimens. All the specimens were lightly etched, washed, and dried so as to give comparable surface finishes before working.

A two-high 10 in. \times 10 in. mill was used for the rolling tests, variations in the frictional conditions being obtained by the use of either chilled-iron or forged-steel rolls, in conjunction with different lubricants. Wire-drawing tests were carried out using a 12-in. bull block, with a drawing speed of 200 ft./min. Three sets of hardened steel dies, with die angles of 12°, 20°, and 30°, were used, and the wire was drawn either dry or with soap lubrication.

2. TESTING OF SPECIMENS

Samples for hardness testing were cut from the centre of each worked specimen, care being taken to avoid overheating during cutting. These were

mounted and were polished on emery paper, finishing with 0000 grade. Wire samples, mounted longitudinally, were ground down until the core of the wire was fully exposed. Copper specimens were polished electrolytically and tested in the polished state. Brass, aluminium, and steel specimens were polished carefully by hand and were etched before testing.

Hardness traverses were made across the specimens, using either a Bergsman or a Cooke, Troughton, and Simms microhardness tester. The techniques necessary for accurate hardness measurements have been discussed by the designers of these instruments^{17, 18} and by one of the present authors.¹⁹ Comparative tests carried out with the two instruments gave the same results. Each point shown on the inhomogeneity curves is the arithmetic average of five hardness indentations. Tests showed the reproducibility to be such that the average of the coefficients of variation of fifteen groups of five tests, chosen at random, was 2.1%.

III.—EXPERIMENTAL RESULTS

1. INHOMOGENEITY IN COPPER ROLLED UNDER STANDARD CONDITIONS

A number of annealed copper samples were given varying reductions, using the chilled-iron rolls scoured

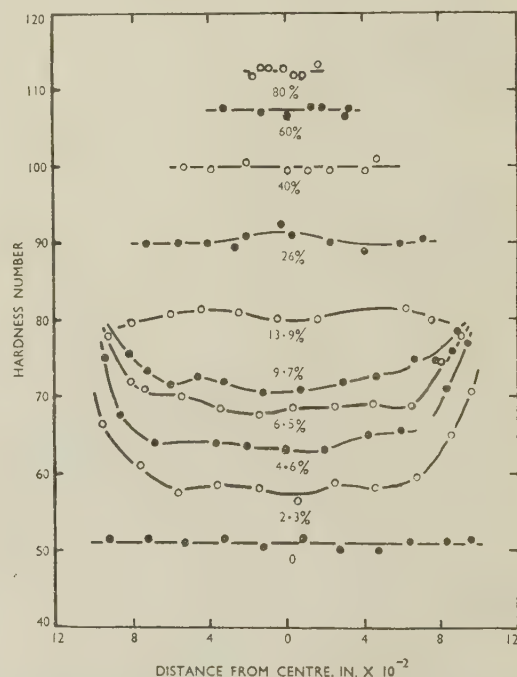


Fig. 1.—Hardness Variations Through the Thickness of Copper Rolled under Standard Conditions. The percentage reduction is indicated on each curve.

with grade 0 emery paper and lubricated with paraffin. The rolling speed was 85 ft./min., and all reductions were obtained in a single pass. These were the basic conditions for all rolling experiments.

The results of microhardness traverses made across polished sections of these samples (Fig. 1) show that reductions up to 13% give rise to preferential work-hardening of the surface layers. As the reduction in thickness increases to this value, the difference in hardness between the surface layers and the core decreases. In most cases, the curves are not smooth, there being superimposed on the main effect a "minor" or "secondary" inhomogeneity in the form of two small protuberances on the curve, between the core and the rolled surface, in agreement with the work of Harris¹¹ and of Collins and Honeycombe.¹³

It was not usually found possible to obtain a reliable hardness value within 80 μ of the rolled surface, but,

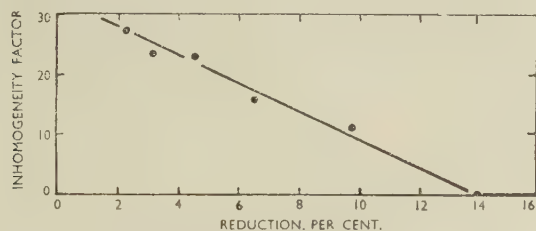


FIG. 2.—The Variation of Major Inhomogeneity with Reduction.

for comparison, all curves were extrapolated to a point corresponding to the worked surface, and the hardness at this point was assumed to be the surface hardness of the sample.

The degree of inhomogeneous deformation can be given a numerical value by expressing the difference in hardness between the core and the surface as a percentage of the core hardness. This value, which will be referred to as the "inhomogeneity factor", is plotted against the rolling reduction in Fig. 2.

In some further experiments, a copper sample was given a reduction in thickness of 50%, the power supply was then interrupted, and the mill allowed to

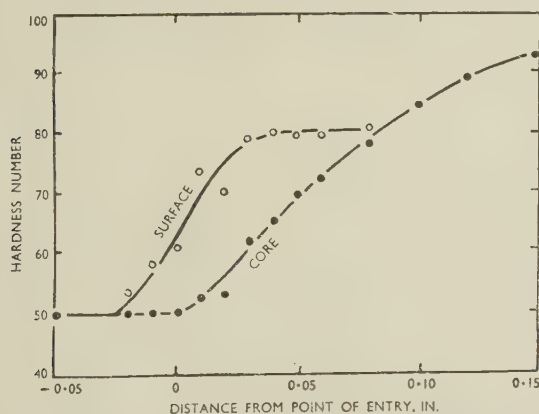


FIG. 3.—The Increase in Surface and Core Hardness Through the First Part of the Arc of Contact of a Copper Specimen Rolled 50%.

come to rest. The rolls were opened and the partly rolled sample was withdrawn. Microhardness traverses made across a section through the arc of contact revealed (Fig. 3) that inhomogeneity persisted for a

short distance past the point of entry. Beyond this point, which was equivalent to 14% reduction, the deformation was substantially homogeneous. Another interesting point shown by this test is that, although the sample was homogeneous before rolling, slight surface-hardening was introduced before the metal entered the roll gap.

2. INHOMOGENEITY IN OTHER METALS ROLLED UNDER STANDARD CONDITIONS

A number of samples of brass, commercial-purity aluminium, and mild steel were rolled under the same conditions as those previously described. The results for brass (Table II) show that the range over which

TABLE II.—The Effect of Rolling Reduction on the Inhomogeneity Factor of 70 : 30 Brass.

Rolling Redn., %	Core Hardness	Surface Hardness	Inhomogeneity Factor
4.5	87	100	15
8.5	98	109	11
14	107	107	0
21	119	119.5	0
33	148	148	0

inhomogeneity exists is approximately the same as for copper. Some inhomogeneity could be detected in aluminium samples given small reductions, but because of the low rate of work-hardening, it could not be accurately measured.

Some hardness measurements on mild steel showed that, when measurements were made immediately after rolling, appreciable inhomogeneity occurred. On ageing for a few days at room temperature, however, these effects disappeared, and the centre of the strip strain-aged to give hardness values similar to those at the surface. No further observations were made on this phenomenon, but it is one obviously worth closer investigation.

3. FACTORS INFLUENCING THE INHOMOGENEITY OF ROLLED METALS

When it became clear that the method of investigating inhomogeneity by microhardness testing was quite successful, it seemed appropriate to investigate the effect of a number of variables on inhomogeneity during rolling and wire-drawing. In the first place it was of some interest to determine whether a metal normally showing inhomogeneity after small rolling reductions would do so if it were initially pre-strained so as to give a higher yield strength.

A number of tensile test-pieces of annealed copper were pre-strained in tension by various amounts so that each sample had a different yield strength. The five specimens were then rolled 5% with the following results :

Tensile Pre-strain, %	Inhomogeneity Factor
0	24
6.6	5
10.4	4.5
16.1	0
18.8	0

Examination of the results shows that pre-straining the material has a definite effect on the degree of inhomogeneity in the final product. No inhomogeneity was caused by rolling when the copper was pre-strained uniformly to a reduction of 15% or more.

The survey of previous work had indicated that the frictional conditions during working might affect the homogeneity of plastic deformation, and a series of confirmatory experiments was carried out on copper under the conditions given in Table III. Fig. 4

TABLE III.—*Rolling Conditions Giving Rise to Different Coefficients of Friction.*

Conditions of Rolls	Conditions of Copper Specimens	Coeff. of Friction *
Scoured with grade 0 emery paper and degreased with trichlorethylene and magnesia.	Dry and degreased	0.19
Scoured with grade 0 emery paper. Paraffin lubrication.	Swabbed with paraffin	0.13
Scoured with grade 00 emery paper. Rolling oil lubrication.	Swabbed with oil	0.07
As above.	Covered with a layer of solid sodium stearate soap	0.04

* The coefficient of friction was estimated by the "limiting draft" method and these numerical values are only very approximate.

shows that the inhomogeneity is reduced by lowering the coefficient of friction, and this dependence on frictional conditions was observed in all the tests.

Other possible variables in the rolling process are the rolling speed and the stock size. To determine

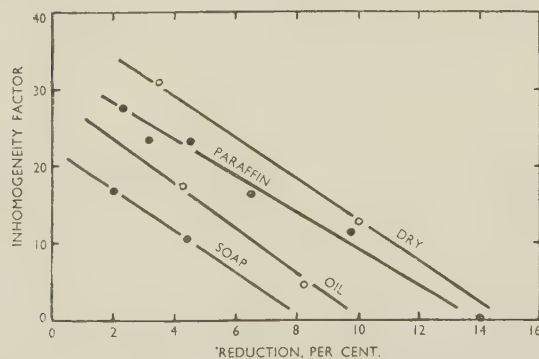


FIG. 4.—The Effect of Alteration in the Frictional Conditions on the Inhomogeneity Factor of Rolled Copper.

whether there was a speed effect, three samples of copper were given a reduction of 4% at rolling speeds of 85, 180, and 250 ft./min. The results showed that, as the rolling speed was increased, the surface hardness, and hence the inhomogeneity, decreased:

Speed of Rolling, ft./min.	Inhomogeneity Factor
85	25
180	19
250	8

The results for 0.8-in. copper bar are shown in Table IV. When the results were compared with those for

TABLE IV.—*The Effect of Rolling Reduction on the Inhomogeneity Factor of 0.8-in.-Thick Copper Specimens.*

Rolling Redn., %	Core Hardness	Surface Hardness	Inhomogeneity Factor
1.2	53	66	25
3.6	58.5	73.5	26
8.7	70	78	11
13.4	76	80	5

standard size (0.2 in.) stock (Fig. 1), the core hardness of the thicker material proved to be somewhat lower, and as the surface hardness was approximately the same, it appeared that an increase in the stock

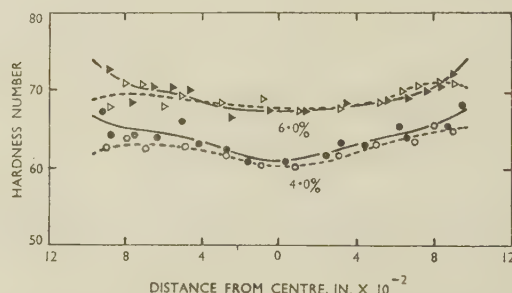


FIG. 5.—The Effect of Reversing the Direction of Rolling on the Inhomogeneity of Copper. The reduction is indicated below each pair of curves and the broken line indicates that the rolling direction was reversed for the second pass.

thickness led only to a slight increase in the degree of inhomogeneity.

The literature of rolling contains some references to the effect on the properties of the final product of several small passes instead of one heavy reduction. To determine whether the degree of inhomogeneity was affected by the method of reduction, three copper samples were given the same total reduction in thickness (10%) by one, two, or ten passes. The results indicated that an increase in the number of passes from one to ten caused a fall in the degree of inhomogeneity from 12 to 5.

MacGregor and Coffin,⁹ using co-ordinate nets scribed on copper bars, have shown that more uniform straining of the sample results if the direction of rolling is reversed after each pass. One specimen of copper was therefore given a reduction in thickness of 4% in two passes without reversals, while a second specimen was given the same reduction but with the sample reversed end-to-end after the first pass. The same treatment was also given to two other specimens, with a total reduction of 6%. The results obtained (Fig. 5) show that the curves for the specimens which were reversed are different from the normal type of inhomogeneity curve obtained with copper. However, no differences between the two methods of rolling could be detected in samples reduced 12.5% and 25% in thickness.

4. INHOMOGENEITY IN DRAWN WIRE

A number of straight lengths of copper wire were drawn to different reductions, using the three sets of drawing dies (12° , 20° , and 30°). Wire-drawing soap powder was used for lubrication, and each reduction was obtained in a single draw.

Fig. 6 gives the curves obtained when wires drawn through the 30° dies were tested. The distribution of the inhomogeneity was similar to that found in rolled copper and, as in rolling, the inhomogeneity decreased as the reduction became heavier. The

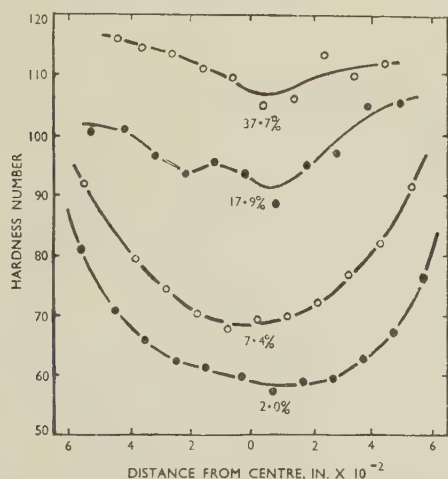


FIG. 6.—Hardness Variations Through the Thickness of Copper Wire Drawn Through 30° Dies. The reduction is indicated below each curve.

results for wire drawn through all three dies, set out in Table V, show that the major inhomogeneity was reduced by a decrease in the die angle. Most wires had regions of secondary inhomogeneity, the effect being most marked at the higher reductions.

TABLE V.—Inhomogeneity in Copper Due to Drawing Through Dies of Various Angles.

Die Angle	Reduction, %	Inhomogeneity Factor	
		Lubricated	Not Lubricated
30°	2	48	52
	7.5	43	45
	18	15	18
	38	6	No test
20°	1.5	18	No test
	10	11	35
	38	0	No test
12°	2	11	No test
	6.5	8	"
	18	0	"

The wire and the dies were then degreased with hot water and trichlorethylene, and drawing was carried out under these conditions. The results obtained are included in Table V. An increase in the coefficient of friction apparently gave rise to a large increase in

the degree of inhomogeneity present in the wire drawn with the 20° die and a negligible increase in wire drawn with the 30° dies. An investigation using the 30° dies and soap lubrication showed that the effect of obtaining the same reduction in area by two draws instead of one was to reduce the inhomogeneity factor from 43 to 20 in one specific case, and an even more uniform specimen, with an inhomogeneity factor of 6, resulted from reversing the direction of drawing after the first pass.

Some mild-steel wires were also tested after ageing and, as with rolling, no major inhomogeneity could be detected, although the secondary inhomogeneity was marked.

IV.—DISCUSSION

The results described in the last section show that there is a very close analogy between the inhomogeneity of deformation in rolling and that in wire-drawing. The only difference lies in the relative magnitudes of the effects, and the two processes will not be treated separately in the following discussion.

1. THE CAUSE OF THE MAJOR INHOMOGENEITY

In any metal-working operation there is friction between the metal surface and the working tool, and the results presented here indicate that it is closely associated with, and is the probable cause of, inhomogeneous deformation and surface-hardening of the metal. The main evidence for this is that the surface-hardening caused by the rolling or drawing of copper was dependent on the frictional conditions and, where good lubrication was achieved, the hardening was appreciably reduced. Confirmatory evidence is provided by the fact that the effect of changes in the working conditions can also be shown to be due to changes in the frictional conditions.

It is generally recognized that lubrication becomes more difficult, and the coefficient of friction increases, as the pressure between the metal and the working tool rises. Thus, increasing the reduction raises the pressure and probably increases the coefficient of friction. Fig. 1 shows, as expected, that the surface-hardening increases with reduction, and a similar effect in drawn wire is apparent in Fig. 6. However, although increasing the reduction raises the surface-hardness, it actually decreases the degree of inhomogeneity, owing to the greater general hardening. A decrease of the die angle in drawing tends to improve the lubrication and to give a corresponding decrease in surface-hardening (Table V).

An increase in rolling speed usually leads to a decrease in the coefficient of friction^{20, 21} and this may be the cause of the marked fall in surface hardness that occurred as the rolling speed was increased (p. 404).

Bowles and Boas²² observed that reversal rolling gave a product which was slightly softer than similar sheet which had been rolled in one direction only.

This is in agreement with the results of the present work (Fig. 5), and can be explained by considering the phenomenon of work-softening. Reversing the direction of rolling reverses the direction in which the frictional forces act, and if these cause plastic deformation, a Bauschinger effect may be expected in the metal, which often gives rise to work-softening.^{23, 24}

It seems from the foregoing that most of the results obtained with copper specimens are self-consistent and that, with reductions up to 14%, a specific surface hardness is associated with certain frictional conditions. When this hardness is attained, further working, under the same frictional conditions, does not lead to any increase in the surface hardness until the bulk of the metal reaches this value. Once this hardness has been reached, the metal hardens uniformly throughout.

Strain-ageing, which occurred during the preparation of steel specimens for hardness testing, obscured the real nature of the deformation, and for this reason no analysis of the results obtained with steel has been attempted.

2. THE CAUSE OF THE SECONDARY INHOMOGENEITY

It was pointed out in Section III that most specimens showed a secondary region of greater hardening

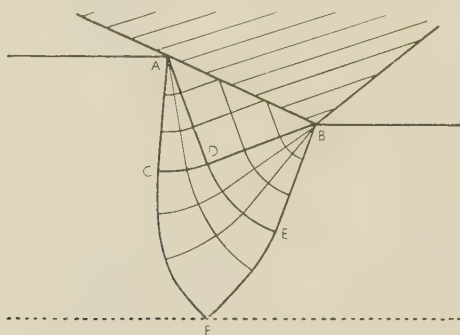


FIG. 7.—A Slip-Line Field Solution for Plane Strain Drawing. (After Hill.²⁵)

midway between the core and the surface. The magnitude of this effect was not affected by variations in the frictional conditions, but its position was found to alter slightly as the geometry of the process was changed; it is therefore probably associated with the manner of deformation during working.

There is no complete analysis of the rolling or wire-drawing processes at present, and Hill's theory of strip drawing²⁵ is not strictly applicable to work-hardening metals. However, examination of his work suggests that deformation is not likely to be uniform and that, neglecting frictional effects, the maximum hardening will not occur at the surface or in the core, but at some midway position. Hill's solution for the plane strain drawing process is shown in Fig. 7; an element passing through this slip-line field will have work done on it, and it can be assumed

that hardening of an element is dependent on this amount of work. As the element crosses the lines *AF*, *AD*, *BD*, and *BF*, it is sheared, and the amount of work done is the angle through which it is sheared. Thus, if the increase in hardness is proportional to the amount of work done, the hardness would be expected to remain constant

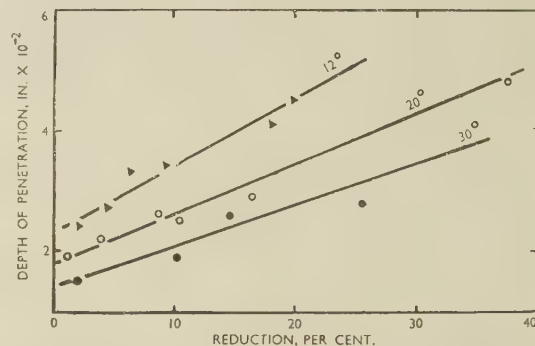


FIG. 8.—The Effect of the Die Angle and Reduction on the Depth of Penetration of Secondary Inhomogeneity in Drawn Wire.

for a certain distance from the surface—about half-way in this case—and then to decrease towards the core. As the element passes through the fields *ADC*, *BDE*, and *CDEF*, other work will also be done, the magnitude of which it is difficult to estimate, though it probably rises to a maximum in the region *CDE*. Thus the maximum hardness might be expected to occur somewhere between the surface and the core of the worked metal. This hypothesis cannot, of course, be applied directly to either rolling or wire-drawing, but the analysis may be qualitatively applicable.

The variation of the depth of the secondary inhomogeneity (taken as the distance from the centre of the protuberance to the surface) with the conditions of working tends to support the idea developed above. Examination of the geometry of Fig. 7 shows that the depth of secondary inhomogeneity in wire should increase with reduction and decrease with die angle, and Fig. 8 shows that these are in fact the results

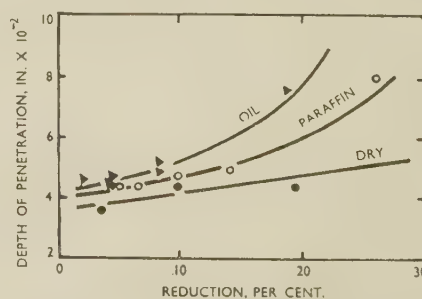


FIG. 9.—The Effect of the Frictional Conditions and Reduction on the Depth of Penetration of the Secondary Inhomogeneity in Rolled Strip.

obtained. Increasing the thickness of the stock in rolling increases the arc of contact for a given percentage reduction, and should thereby increase the depth

of secondary hardening. In a typical case, secondary inhomogeneity was found to occur 0.048 in. from the surface of 0.2 in. stock and 0.128 in. from the surface of 0.8 in. stock. Increasing friction tends to reduce the angle ABD in Fig. 7, and therefore secondary inhomogeneity may be expected to occur nearer the surface with a higher coefficient of friction. Results confirming this are shown in Fig. 9.

Thus, there seems to be considerable evidence in favour of the idea that secondary inhomogeneity is due to what might be described as "geometrical" hardening as opposed to the "frictional" hardening associated with major inhomogeneity.

3. GENERAL DISCUSSION

The work reported here shows that it is possible to control to some extent the degree of inhomogeneity in worked metals. In metals such as copper and brass, surface-hardening is important only at low reductions and can be reduced by improving the lubrication or by reversing the direction of deformation after each pass. There is no surface-hardening in strain-aged mild steel or heavily worked copper, and secondary inhomogeneity should have a relatively minor effect

on the mechanical properties compared with that of the total plastic deformation.

It was pointed out in the introduction that most metal-working operations give rise to undesirable residual stresses which can probably be related to inhomogeneous plastic deformation. No attempt was made in this work to measure residual stresses, but where such difficulties arise it is considered that the results of the present research may be of value in that they would allow procedures to be laid down for modifying the conditions of working so as to lead to less inhomogeneity.

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REFERENCES

1. W. Linicus and G. Sachs, *Mitt. Material., Sonderheft* **16**, 1931, 38.
2. R. G. Treuting, J. J. Lynch, H. B. Wishart, and D. G. Richards, "Residual-Stress Measurements". 1952: Cleveland (American Society for Metals).
3. W. M. Baldwin, *Proc. Amer. Soc. Test. Mat.*, 1949, **49**, 539.
4. R. McC. Baker, R. E. Ricksecker, and W. M. Baldwin, *Trans. Amer. Inst. Min. Met. Eng.*, 1948, **175**, 337.
5. H. Bühler and W. Püngel, *Arch. Eisenhüttenwesen*, 1934, **8**, 165.
6. G. I. Taylor and H. Quinney, *J. Inst. Metals*, 1932, **49**, 187.
7. E. Siebel and H. Hühne, *Mitt. K.-W. Inst. Eisenforsch.*, 1931, **13**, 43.
8. H. Unkel, *Arch. Eisenhüttenwesen*, 1938, **12**, 277.
9. C. W. MacGregor and L. F. Coffin, *J. Appl. Mechanics*, 1943, **10**, A13.
10. M. Cook and G. K. Duddridge, *J. Inst. Metals*, 1939, **64**, 311.
11. F. W. Harris, *Trans. Amer. Inst. Min. Met. Eng., Inst. Metals Div.*, 1928, 518.
12. A. D. Schwoppe, K. F. Smith, and L. R. Jackson, *ibid.*, 1949, **185**, 409.
13. J. Collins and R. W. K. Honeycombe, *J. Council Sci. Indust. Research, Australia*, 1948, **21**, 59.
14. G. Sachs, "Spanlose Formung der Metalle", p. 65. 1931: Berlin (Julius Springer).
15. G. I. Pogodin-Alexeev, *Vestn. Inzhen. Tekhn. (Eng. Tech. Herald)*, 1940, 226.
16. F. C. Lea and R. A. Batey, *Proc. Inst. Mech. Eng.*, 1928, (2), 865.
17. E. B. Bergsman, *Jernkontorets Ann.*, 1945, **129**, 577.
18. E. W. Taylor, *J. Inst. Metals*, 1948, **74**, 493.
19. B. B. Hundy, *Metallurgia*, 1951, **43**, 99.
20. R. B. Sims and D. F. Arthur, *J. Iron Steel Inst.*, 1952, **172**, 285.
21. J. Billigmann and A. Pomp, *Stahl u. Eisen*, 1954, **74**, 441.
22. J. S. Bowles and W. Boas, *J. Inst. Metals*, 1948, **74**, 501.
23. N. H. Polakowski, *J. Iron Steel Inst.*, 1951, **169**, 337.
24. B. B. Hundy and W. A. Backofen, to be published.
25. R. Hill, "The Mathematical Theory of Plasticity". 1950: Oxford (Clarendon Press).

1613 DEFORMATION AND ANNEALING TEXTURES IN THORIUM *

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SYNOPSIS

Pole figures of the sub-surface texture of thorium for various degrees of deformation have been determined, using both qualitative and quantitative methods. In the heavily rolled condition, the texture may be approximately described by four equivalent orientations near (123)[121]. On annealing, a re-orientation of about 40° rotation about a [111] axis takes place, resulting in a fairly well-developed cube texture (100)[001].

It is suggested that the deformation texture normally associated with face-centred cubic metals, viz. (110)[112], is really a transition texture developed from the true face-centred cubic texture of pure metals, viz. (123)[121], by the introduction of solute atoms. This transition depends on the interaction energy of a solute atom and a dislocation in the parent lattice, and occurs only when this energy is sufficient to cause appreciable "atmosphere" locking.

I.—INTRODUCTION

THE potentialities of thorium as a reactor material have prompted an investigation of its physical properties, particularly its alloying and deformation characteristics. Although thorium undergoes a phase transformation,¹ the temperature at which this occurs is so high that the deformation behaviour is determined by the face-centred cubic structure of the low-temperature phase. The present paper describes work on the deformation and annealing textures, which are of interest both from a practical and a theoretical standpoint. Practically, preferred orientation is important because the anisotropy introduced by deformation and annealing may prove troublesome during further fabrication by pressing, cupping, &c. Theoretically, preferred orientation affords an opportunity of considering how far macroscopic behaviour can be predicted from fundamental knowledge on an atomic scale.

The rolling texture of face-centred cubic metals is commonly described as one in which a plane of the form (110) is parallel to the rolling plane and a [112] direction is parallel to the rolling direction.²⁻⁴ This may be written (110)//R.P. [112]//R.D., or simply (110)[112]. The rolling textures of some copper-base alloys, particularly 70 : 30 brass, have been consistently characterized by such an ideal orientation. Certain other face-centred cubic metals, however, e.g. aluminium, copper, and nickel, develop rolling textures rather different from that of brass. These textures have been variously described by the following ideal orientations: (110)[112]; (112)[111]⁵; (135)[533]⁶; (135)[211]⁷; (123)[121]⁸; &c. Most of the discrepancies have usually been attributed to the lack of sharpness in the texture and to the attendant difficulties of associating "ideal" orientations with pole figures showing scatter. It is therefore

essential that pole figures be used to describe the experimental data.

Recrystallization textures^{2,9} are generally the result of annealing material with a pronounced deformation texture, but they are usually not as sharply defined as the deformation textures. Both (113)[211] and (100)[001] orientations have been observed very frequently in face-centred cubic metals and alloys. However, these straightforward textures are sometimes complicated by being mixed with a retained rolling texture and other, intermediate orientations. The pure cube texture (100)[001] has been obtained only in certain face-centred cubic materials: copper, nickel, gold, iron-nickel alloys, and some ternary iron-copper-nickel alloys.

II.—DEFORMATION TEXTURES

1. PREPARATION OF SPECIMENS

Most of the present research was carried out on sintered thorium bar, containing 99.5% total thorium, with calcium 215, iron 55, nitrogen 195, and other elements <10 p.p.m.

The nominal thorium content was obtained by wet chemical methods; other elements were determined spectrographically. The balance unaccounted for is believed to be made up of thorium not detected by the analysis. The strip for the specimens was cold rolled (5% reduction per pass) in a two-high mill, with 8 in. roll dia., using a small amount of mineral lubrication to reduce surface friction. The strips were reversed, end to end, between passes.

Originally, it was intended to determine the deformation and annealing textures of thorium strip deformed 90–95%. However, with the original starting thickness of $\frac{5}{8}$ in., the sintered thorium bar fractured after 60% reduction (strip A), and it was necessary to use thinner starting material to obtain the desired 90%

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reduction without fracture (strip *C*). Strip *B* (80% reduction) was then produced to complete a sequence for the investigation of the development of texture. Strip *D*, compression-rolled material, i.e. rolled with many passes, each pass in a different direction, was chosen for study because experimentally this texture is simpler to determine and a real connection exists between the compression texture and the complete rolling texture (see Section II, 3). Resintered material, used as the basis for strip *E*, was prepared by sintering thorium powder (thoria 0.9, carbon 0.02, iron 0.05%, with traces of calcium and magnesium) at 1300°C., rolling to 50% reduction, and then resintering at 1300°C. before a final reduction of 95%.

X-ray specimens were prepared by cutting sections from the centre of the strip. Except when the surface texture was required, all specimens were examined after electropolishing in a bath containing perchloric acid 10, ethyl alcohol 45, and butyl cellosolve 45%, at a c.d. of 1.5 amp./cm.². Polishing was usually continued for 10–15 min. to remove all trace of surface effects and strain. The measured depth removed was of the order of 0.005–0.01 in.

2. EXPERIMENTAL TECHNIQUES

A difficulty associated with the study of preferred orientation in thorium is the heavy absorption of X-rays of wave-length suitable for diffraction work. The normal transmission method, ordinarily the most useful, is thereby ruled out. A modification of this method, discussed by Winogradski¹⁰ for uranium, could have been employed, but the preparation of extremely thin sections of thorium by etching is experimentally tedious, and a glancing-angle, or reflection, technique was therefore adopted.

Three entirely different experimental reflection techniques were used, one photographic and two involving a Geiger-counter. Copper K_{α} radiation was used throughout. A photographic method was applied to obtain an overall picture of the pole figures, while with the Schulz reflection Geiger technique (described below) a particular area of the pole diagram could be investigated with greater accuracy. The third reflection technique, a comparative one, was found to be both useful and relatively rapid for comparing the texture from specimen to specimen.

(a) Photographic Method

The photographic technique used for the investigation of uranium,¹¹ and now applied to thorium, is based essentially on a method developed by Custers.¹² A flat sample is placed at an angle θ_{hkl} to the X-ray beam, and a glancing-angle photograph of the hkl reflection is obtained on a flat photographic film. The specimen is rotated in steps about the normal, and a photograph obtained at each position. The observed angular extent of the maxima and minima of intensities are plotted on a circle of reflection which passes through the centre of the standard stereo-

graphic projection, the normal to the face of the specimen being at the centre of the projection. Fig. 1 shows a series of circles of reflection corresponding to 15° rotations for the reflection $\theta_{hkl} = 17^\circ$. These circles can be used for the 111 and 200 reflections of thorium. In the present work, the X-ray photographs were taken in a scanning camera¹³ to eliminate "spottiness" of the lines. Owing to the shadow cast by the specimen and holder, only about 120° of the Debye-Scherrer arc appeared on the film. It was therefore possible to make three different exposures, corresponding to stepwise rotations of the specimens, on the same circular film. Positions of the intensity

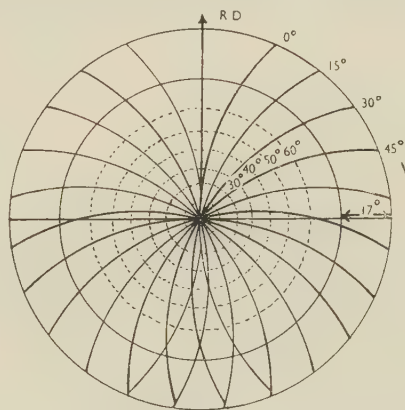


Fig. 1.—Chart for Plotting Pole Figure from Photographic Data ($\theta = 17^\circ$). The angular extent of the film arcs is plotted along curves passing through the centre of the stereogram.

maxima were read directly from the X-ray photographs by means of a protractor, and transferred directly to the pole figure using the chart described (Fig. 1). Three prepared surfaces of the sample, perpendicular respectively to the rolling direction (R.D.), to the transverse direction (T.D.), and to the normal direction (N.D.), were examined to afford a substantial coverage of the pole figure.

(b) Quantitative Geiger-Counter Method

The method adopted here is based essentially on one proposed by Schulz¹⁴ for use with a flat sample. This appears to be the most convenient method, since no corrections for absorption or change in geometry during rotation of the specimen are necessary.

In the Schulz arrangement (Fig. 2 (a)) the specimen is fixed to a rotatable mount with its reflecting surface perpendicular to the axis of rotation. Rotation of the specimen around this axis is denoted by the angle α . The collimating system, consisting of slits S_1 and S_2 , gives negligible divergence in the vertical direction. Slit S_2 permits radiation to strike only a narrow portion of the specimen, while S_3 , the detector slit, limits the length of the Debye-Scherrer arc entering the Geiger-counter. Thus, the X-rays passing the aperture slit S_1 and the main slit S_2 are reflected

from the specimen and focused at the receiving slit S_3 .

The specimen, together with the mounting table, can be rotated about an axis $X-X$, which is in the reflecting surface. This rotation is carried out by changing the relative positions of the inner ring (2) and outer ring (3). The angle of rotation ϕ determines the distance of the reflecting pole P (Fig. 2 (b)) from the centre of the pole figure (N.D.) along one diameter. The setting of the specimen on its rotatable mount, given by the angle α , alters the diameter. Thus, by means of the counter, the reflected X-ray intensity can be measured, over the complete pole figure, as a function of ϕ and α .

The experimental arrangements for the Schulz

used previously as a rapid method of estimating the amount of preferred orientation in a sample.^{15, 16} If I_{hkl} is the measured intensity of the hkl reflection from an oriented sample and A_{hkl} is the intensity of the same reflection from a random sample, a quantity p is defined as:

$$p = \frac{I_{hkl}}{\Sigma I_{hkl}} \cdot \frac{\Sigma A_{hkl}}{A_{hkl}}$$

where ΣI_{hkl} and ΣA_{hkl} are the sums of all the measured intensities from an oriented and random sample, respectively. The quantity p is a measure of the abundance of the (hkl) planes parallel to a particular surface of the sample, relative to that for a random distribution. Thus $p = 1$ for a random distribution

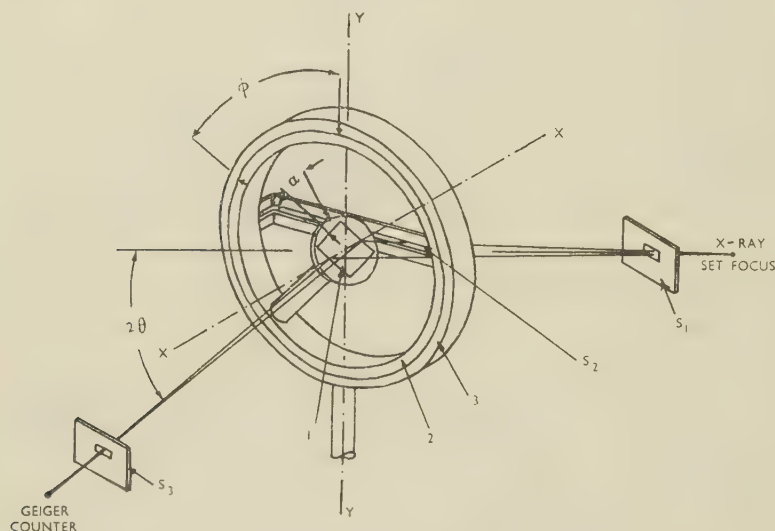


FIG. 2 (a).—Diagram Showing the Principle of the Schulz Reflection Geiger Technique.

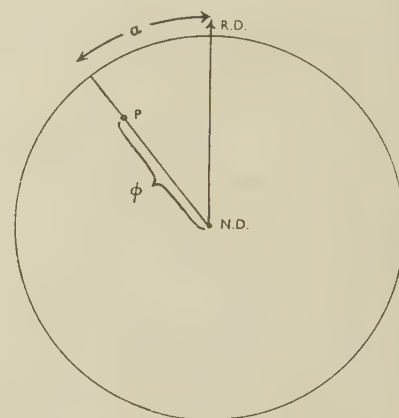


FIG. 2 (b).—Pole Figure Showing the Position of Pole P as Determined by ϕ and α .

reflection Geiger technique are shown in Fig. 3 (Plate LXII). Although theoretically the method can produce a complete quantitative pole figure, in the present work it was found that the useful range of ϕ was limited by defocusing effects, for beyond about 60° from the centre of the pole figure the measured intensity rapidly decreased. Consequently, since for the peripheral part of the pole figure "drop-off" corrections would have to be allowed, the method was used to record pole densities only within 60° of the normal to the face being investigated. To ensure that the results were representative of the sample, the specimen-holder was equipped with a scanning device. The intensity measurements were in most cases taken at 10° intervals of rotation of the specimen in its own plane, and at 5° intervals of rotation of the specimen about axes in the plane of rolling. In high-intensity regions, readings were taken at closer intervals.

(c) Comparative Geiger-Counter Method

This method is essentially one in which the integrated intensities from a rolled sample are compared with those from a randomly oriented one. It has been

(ΣI_{hkl} and ΣA_{hkl} are normalized), $p < 1$ indicates a deficiency and $p > 1$ an excess of particular planes parallel to the surface.

The method is rapid and reasonably accurate when the degree of preferred orientation is not very high.

TABLE I.—Normalized Intensity Values for Various Crystallographic Planes in Randomly Oriented Thorium.

Line	$\frac{A}{\Sigma A}$ Values	
	Calculated	Measured
111	0.363	0.340
200	0.186	0.234
220	0.129	0.115
311	0.149	0.160
222	0.042	0.039
400	0.019	0.021
331	0.058	0.049
420	0.053	0.042
Σ	1.000	1.000

However, the errors in absolute p values become appreciable when the sample is highly oriented, owing to the relatively small number of strong reflections observed. The calculated p values are probably not accurate to better than 15%. The values of A_{hkl} for the calculation of the p values were both calculated and measured. The normalized values are shown in Table I.

3. EXPERIMENTAL RESULTS

(a) Rolling Textures

Figs. 4 (a) and (b) show, respectively, the (111) pole figures qualitatively determined for the sub-surface texture of sintered thorium rolled 80 and 90%.

cubic metals. The (112)[11 $\bar{1}$] orientation previously proposed accounts approximately for the central maxima, but the remaining (111) poles for this orientation do not fit the intensity maxima found in other regions of the pole figure. The present results are, however, in fairly good agreement with the other previously proposed orientations, particularly (135)[21 $\bar{1}$] and (123)[$\bar{1}21$].

Using the Schulz reflection technique, the high-intensity area near the centre of the pole figure was investigated more closely to determine the actual peak position. Fig. 7 (a) shows the central portion of the (111) pole figure quantitatively determined for sintered thorium rolled 90%. Fig. 7 (b) shows the complete (111) pole figure quantitatively determined

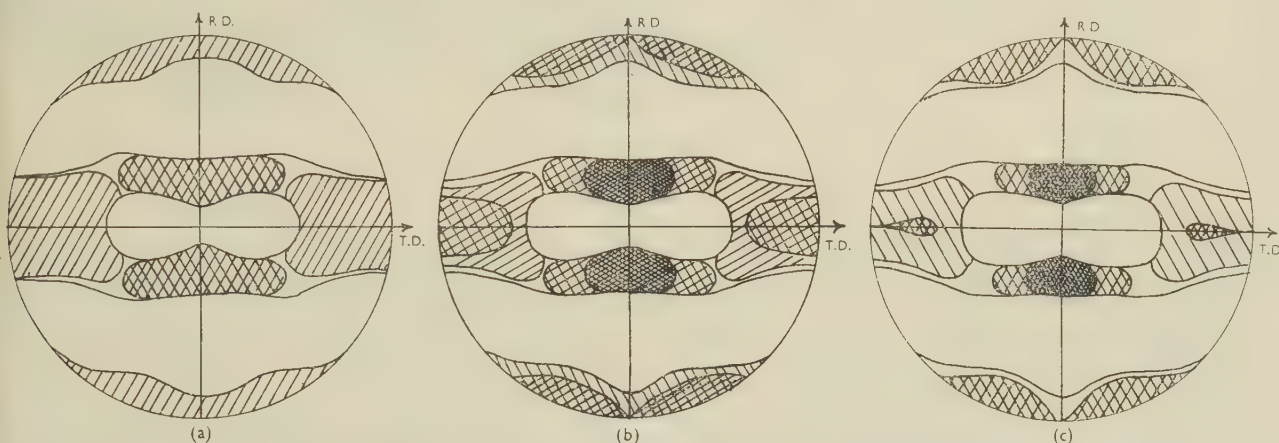


FIG. 4 (a)-(c).—(111) Pole Figures, Qualitatively Determined, for Sub-Surface Textures of: (a) Sintered Thorium Rolled 80%; (b) Sintered Thorium Rolled 90%; (c) Resintered Thorium Rolled 95%.

80% deformation is sufficient to give a fairly well developed texture, but, as expected, the scatter is reduced by the extra 10% rolling. Several regions of high density occur, particularly the symmetrical regions located 20°–40° from the centre of the pole figure towards the rolling direction. The (111) pole figure for resintered thorium rolled 95% (Fig. 4 (c)) indicates little significant change from that for the sintered thorium rolled 90%; the scatter around the high-intensity regions is slightly reduced. The (200) pole figures for all the thorium specimens were similar, but showed slightly more scatter than the (200) pole figure for the specimen rolled 95% (Fig. 5).

Although an attempt has been made to assign an ideal orientation to the pole figures obtained, there are difficulties associated with this practice, since different observers ascribe different indices to textures which are fundamentally the same, owing to the lack of sharpness of the diagrams. This is the chief reason for using pole figures. The (111) pole figure showing "ideal" orientations used by other workers for various face-centred cubic metals and alloys is given in Fig. 6. The high-intensity region, near the centre of the stereograms (Fig. 4), observed in the thorium texture, does not appear to be satisfactorily accounted for by (110)[$\bar{1}12$], the principal orientation for face-centred

for resintered thorium rolled 95%. The central maximum in both instances is an extremely sharp high-intensity one, and is located at 25° from the centre towards the rolling direction in the first case

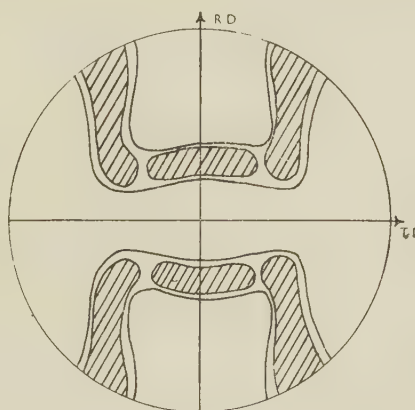


FIG. 5.—(200) Pole Figure for Resintered Thorium Rolled 95%.

and at about 26°–27° in the second. Neither (135)[21 $\bar{1}$] nor (123)[$\bar{1}21$] describes this peak, or the whole pole figure exactly (although (123)[$\bar{1}21$] is the nearer), and it appears that some high-numbered

irrational indices are required. However, since the exact indices are of little significance, the textures can be approximately described by four "ideal" orientations close to $(123)[\bar{1}\bar{2}1]$.

Values of p obtained by measuring integrated line intensities from samples rolled 60, 80, 90, and 95% are given in Table II. A specimen with an (hkl) p

and compression textures, as though the rolling process could be considered as the combination of elongation in the rolling direction and compression normal to the rolling plane.¹⁷ The more simply determined compression texture therefore affords an interesting basis for comparing face-centred cubic rolling textures.

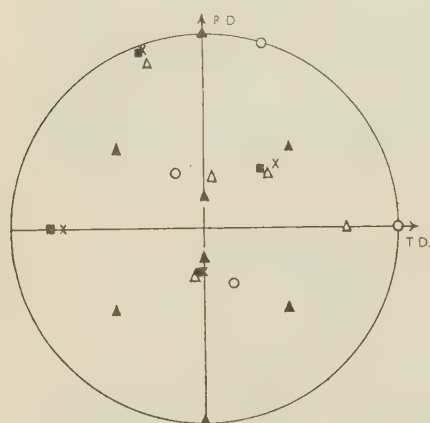


FIG. 6.—(111) Pole Figure Showing Ideal Orientations Used by Previous Workers.

KEY.
 ○ (110)[$\bar{1}\bar{1}2$. ▲ (112)[$\bar{1}\bar{1}\bar{1}$.
 × Near (123)[$\bar{1}\bar{2}1$. ■ (135)[$\bar{5}3\bar{3}$.
 △ (135)[$\bar{2}\bar{1}\bar{1}$.

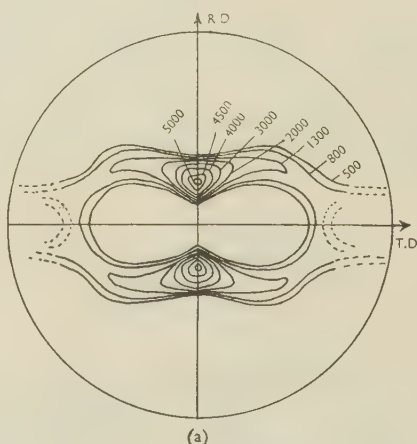
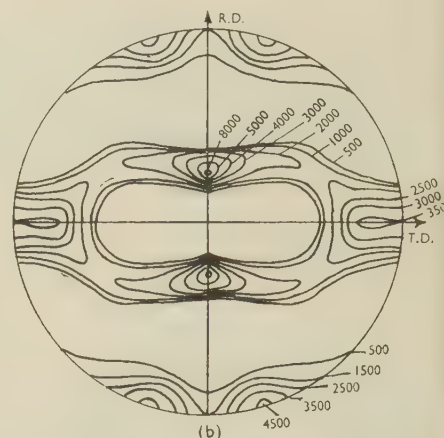


FIG. 7.—(a) Central Portion of (111) Pole Figure, Quantitatively Determined, for Sintered Thorium Rolled 90%; (b) Complete Pole Figure, Quantitatively Determined, for Resintered Thorium Rolled 95%. (Intensities in arbitrary units.)



value greater than unity indicates an excess of that particular plane, relative to a random sample, parallel to the surface examined. A p value less than

Values of p for the compression textures after 95% reduction of 70:30 brass, copper, and sintered thorium (strip D) have been determined (Table III). Fig. 8 ($a-c$) shows the results presented on a unit triangle of a standard stereographic projection.

TABLE II.—Estimated Values of p for Cold-Rolled Thorium.

Deformation, %	Surface Examined Perpendicular to:	Surface Condition	(hkl) p Values					
			111	200	220	311	331	420
60	N.D.	Electropolished	0.26	1.56	1.81	1.55	1.46	1.15
80	N.D.	As rolled	0.28	1.4	1.55	1.61	0.3	0.4
	"	Electropolished	0.12	1.0	2.4	1.95	0.6	0.95
	R.D.	"	1.1	1.5	0.7	1.03	0.48	0.41
	T.D.	"	1.4	0.8	0.8	0.91	0.35	0.7
90	N.D.	As rolled	0.3	1.2	2.0	0.55	0.25	0.27
	"	Electropolished	0.13	0.8	3.52	2.01	0.0	0.4
	R.D.	"	1.4	1.5	0.0	1.03	0.35	0.38
	T.D.	"	1.2	0.67	1.8	0.55	1.1	0.38
95	N.D.	As rolled	0.28	2.0	1.65	1.61	0.32	0.6
	"	Electropolished	0.05	1.03	3.51	1.83	0.31	0.35

unity indicates a deficit. Values for the as-rolled condition and after removing the surface layers by electropolishing indicate that the (100) plane is more predominant in the surface layers than in the bulk of the material.

(b) Compression Rolling Textures

It has been often suggested that a connection exists between rolling textures and the simple tension

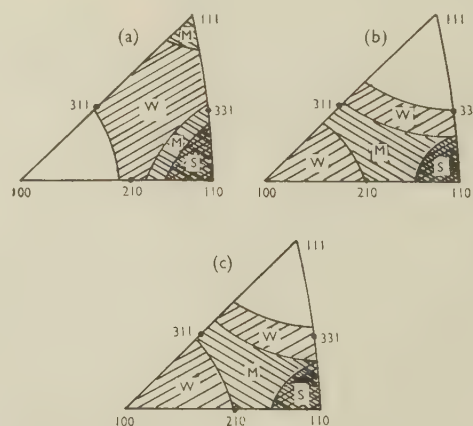


FIG. 8.—Compression Rolling Textures for: (a) 70:30 Brass; (b) Copper; (c) Thorium.

W = weak. M = medium. S = strong.

Possible contour lines for the spread of orientation are included, and the diagrams for copper and α -brass agree fairly well with those previously determined.¹ The compression textures for copper and thorium are

similar and exhibit an absence of orientations around [111], a near absence around [100], and a concentration around [110]. The texture of 70:30

rolled 60, 80, and 90% and resintered thorium rolled 95%, are given in Table IV. The results quoted are from the surface perpendicular to the normal direction, i.e. in the rolling plane.

TABLE III.—Values of p for Compression-Rolled Specimens.

Material	(hkl) p Values					
	111	200	220	311	331	420
α -Brass .	1.4	0	2.6	0	0.1	0.3
Copper .	0	0.6	5.2	1.4	0.2	0.7
Thorium .	0	0.7	3.5	1.9	0.2	0.5

brass, which has a true (110)[$\bar{1}12$] rolling texture, is different, however. No crystallites of α -brass have [100] directions near the axis of compression, while a fair number have [111] in this region; the concentration around the [110] position is still predominant.

III.—ANNEALING TEXTURES

1. EXPERIMENTAL PROCEDURE

In determining the annealing texture of rolled thorium, specimens were taken from each of the strips previously used. Before the annealing texture was developed, the approximate recrystallization temperature was determined. A number of specimens were cut from the stock rolled 90% and annealed *in vacuo* for 10 min. at intervals in the range 0°–1300° C. Vickers hardness measurements were made on each electropolished annealed specimen, and the average of four readings was plotted as a function of temperature. The results showed a fall in hardness from the rolled value of 130 to 78 V.P.N. at 550°–600° C.

The texture was examined for each material annealed at 1000° C., while that for the stock rolled 90% was re-investigated after annealing at 700° C. The preparation of the specimens for X-ray diffraction was carried out as described previously. The average recrystallized grain-size after annealing, as determined on specimens electrolytically etched in 50:50 acetic acid/phosphoric acid solution, was about 0.01 mm.

2. EXPERIMENTAL RESULTS

The (200) pole figure for thorium rolled 90% and annealed, determined photographically, showed a fairly well-developed (100)[001] orientation or cube texture. The (200) pole figure for thorium rolled 90 or 95% and annealed was also determined by the Schulz reflection technique. The results merely confirmed the film measurements and the quantitative pole figures are not reproduced here. However, Fig. 9 shows a curve of intensity plotted against ϕ (see Fig. 2 (b)) for the specimens rolled 90% and annealed, taken along the rolling direction. The variation of intensity with ϕ for the other directions, e.g. the transverse direction, was similar. Some of the p values obtained on annealing the sintered thorium

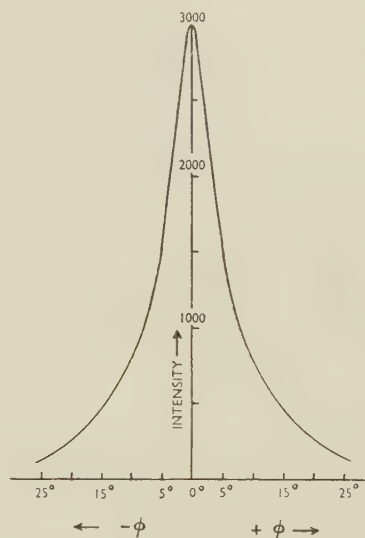


FIG. 9.—Curve of Intensity Against ϕ , Taken Along the Rolling Direction, for Thorium Rolled 90% and Annealed for 10 Min. at 1000° C.

The (200) p value is a good indication of the alignment of the cube texture. The variation of cube texture with temperature appears to be insignificant,

TABLE IV.—Values of p for Cold-Rolled and Annealed Thorium.

Deformation, %	Annealing Temp., °C.	(hkl) p Values					
		111	200	220	311	331	420
60	1000	0.3	1.5	1.9	1.5	0.9	1.7
80	1000	0.48	2.0	0.88	0.92	0.78	1.1
90	700	0.5	2.5	0.91	0.72	0.7	0.7
	1000	0.6	2.5	0.89	0.9	0.9	0.85
95	1000	0.4	3.0	0.6	0.6	1.0	1.2

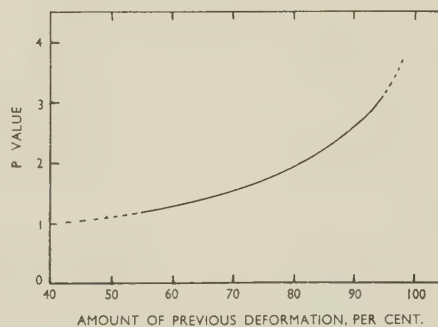


FIG. 10.—Variation of Cube Texture with Amount of Previous Deformation in Cold-Rolled Thorium Subsequently Annealed.

but the variation with amount of previous deformation by cold rolling is appreciable, and is illustrated in Fig. 10.

IV.—DISCUSSION

1. DEFORMATION TEXTURES

For compression rolling the texture of thorium is essentially [110] with a spread to [100] and [311]. Comparative experiments show that this is similar to the texture developed in copper, but markedly different from that of 70:30 brass, where [110] is again predominant but has a spread to [111] and [311] and some concentration at [111].

The straight rolling texture, the pole figure for which was checked by direct quantitative determinations, is also very similar to that described by Hu, Sperry, and Beck¹⁸ for copper and 2S aluminium. It may be expressed roughly as four equivalent orientations not very far from (123)[121], but the texture can be described adequately only by reference to the actual diagram. The high-intensity maxima near the centre of the pole figure at 25°–27° do not agree precisely with the observed positions, 22° for copper and 25° for aluminium, reported by Hu *et al.*¹⁸ Such variations may be due to minor differences in slip behaviour in these materials, but they are more likely to be a consequence of slight experimental variation in rolling procedure. Although the surface texture of thorium has not been examined in detail, from comparative measurements made parallel to the strip surface it appears to differ from the inside texture, the (100) plane being more dominant in the outer layers.

Several treatments initiated by Taylor¹⁹ have been put forward to enable deformation textures to be predicted from a knowledge of the deformation modes of the metal, i.e. the slip and twinning characteristics. Calnan and Clews,²⁰ on the basis of a number of assumptions which reduce the labour of calculation of the previous treatments, have made stereographic plots of the general trends of crystal rotation, to account for the observed orientations resulting from tension, compression, and rolling. The predictions of the treatment for face-centred cubic metals, where the mechanism of plastic deformation is taken to be glide on the octahedral planes in the direction of the face diagonals, were compared with the ideal rolling orientation (110)[112]. However, these authors' diagrams,²⁰ giving the predicted orientations for compression and rolling processes, account very satisfactorily for the observed textures in thorium, as well as in such metals as copper and aluminium.

It therefore appears that the textures to be expected in face-centred cubic metals are those observed in copper or aluminium and that the so-called "ideal" orientation exhibited by 70:30 brass really constitutes an exceptional case. Taking this point of view, an examination of the textures observed by previous workers in face-centred cubic materials has been made (see Table V). The results indicate that the (110)[112] rolling texture, previously considered to be the ideal orientation for face-centred cubic metals, is obtained only in face-centred cubic

alloys. Thus the (110)[112] type appears to be a transition texture brought about by the addition of a second element to the parent metal. Evidence for this difference in texture can be found if one compares, say, copper and α -brass. Although copper and α -brass exhibit the same deformation modes, i.e. slip on the {111} planes in the $\langle 110 \rangle$ directions, they have totally different slip characteristics. For example, copper has a parabolic stress/strain curve,

TABLE V.—Experimentally Determined Deformation Textures in Face-Centred Cubic Materials.

Method of Deformation	Material	Texture	Reference
Compression rolling	Aluminium	[110] with a spread to [100] and [311]	Barrett ²
	Nickel	" " "	" (also present work)
	Copper	" " "	Present work
	Thorium 70:30 Brass	[110] with a spread to [111] and [311] and some concentration at [111]	Barrett ² (also present work)
Rolling	Aluminium	Scatter around orientations (123)[121] near	Beck and Hu ²⁸
	Copper 70:30 Brass	(110)[112] "	" "
	Thorium	Copper-type	Present work
	Copper-5% zinc	Brass-type	Brick, Martin, and Angier ²⁷
	Copper solid solutions with various additions of Mn, Al, As, Sb, Si, Mg, Sn	"	" " "
	Copper-nickel (0–100%)	Copper-type	" " "
Compression	Copper-cobalt	"	" " "
	Nickel	"	" " "
Compression	Copper solid solutions with >1% Al, >5% Zn, <30% Ni	[110] with a spread to [100] and [311]	Hibbard and Trout ²⁸
	Cu solid solutions with >2% Al, >8% Zn	[110] with spread to [111] and [311] and some concentration at [111]	" " "

whereas α -brass shows evidence of yielding and associated phenomena such as "easy glide."²¹ Moreover, the hardening characteristics of the two materials are entirely different; in copper the slip planes harden equally, while in α -brass the active slip planes harden less rapidly than the inactive ones.²²

Recent theoretical work by Calnan²³ has shown that, on a grain-rotation basis, the difference in hardenability of slip planes can account for the two possible textures. However, since yield behaviour, easy glide, and hardenability are all interrelated,^{24, 25} it is probable that the fundamental cause of the transition lies in the interaction of solute atoms and dislocations in the parent lattice. Some support for this view can be obtained from Table V, where it can be seen that zinc solute atoms are effective in producing a complete (110)[112] texture, whereas nickel atoms are not. Presumably, the binding energy between zinc and a dislocation in the copper lattice (approximately $\frac{1}{8}$ eV.) is sufficient, while that of nickel (approximately $\frac{1}{16}$ eV.) is too low.

Several experiments relating texture transition to solute interaction will be reported later.

2. ANNEALING TEXTURES

The preferred orientation obtained on rolling and subsequent annealing, as reported in Section III, 2, is the (100)[001] or "cube" texture. The necessary re-orientation of the structure which has taken place on annealing can best be seen from Fig. 11. It is evident that each of the four [111] axes of a cube orientation approximately coincides with a [111] axis of each of the four orientations of the rolling-texture components. Thus, the cube orientation is related to each of the four (123)[$\bar{1}\bar{2}\bar{1}$]-type orientations by a [111] rotation of approximately 40° . Such an

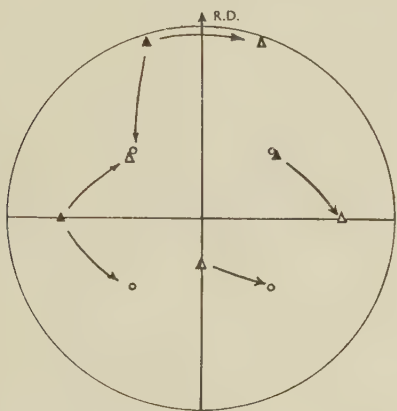


FIG. 11.—Illustrating Re-Orientation of Structure on Annealing Cold-Rolled Thorium. An orientation relationship is evident between two (123)[$\bar{2}\bar{1}\bar{1}$]-type orientations (open and solid triangles) and the (100)[001] orientation (open circle). A (111) pole of each (123)[$\bar{2}\bar{1}\bar{1}$]-type orientation (rolling-texture component) and a (111) pole of the cube texture, nearly coincide. The cube texture can be derived from either of the four components of the rolling texture by a [111] rotation of between 30° and 40° .

orientation relationship has previously been noted on several occasions,²⁶ particularly in aluminium and copper.

Barrett,²⁹ in 1940, pointed out that this orientation relationship may be a result of the orientation-dependence of the rate of grain-boundary migration. More recently, considerable evidence has become available in favour of this view;³⁰ for example, it is now known that the rate of grain-boundary migration is strongly dependent on the relative orientation of the two grains meeting at the boundary. In general, the mobility is very low for boundaries between grains of nearly identical orientation, or for coherent twin boundaries, while the boundaries between the grains of a relative orientation corresponding to a [111] rotation of 30° – 40° have the highest mobility in face-centred cubic metals.

Using arguments based entirely upon this orientation-dependence of grain mobility, i.e. the oriented-growth theory, Beck³¹ has accounted for the (100)[001] cube texture. He also ascribes the absence of cube textures in some face-centred cubic material, notably 70 : 30 brass, to the change in the deformation texture. In such cases the annealing texture is related to the rolling texture by a [111] rotation of about 30° , but because of the different initial rolling texture, it develops no cube-texture component.

Finally, Fig. 10 indicates that the percentage of cubically aligned grains depends, as previously reported by Baldwin,³² on the amount of previous deformation introduced by rolling. Beck²⁶ has also accounted qualitatively for similar results in copper by stating that the cube texture develops earlier in the annealing process, when greater opportunity exists for contact with all four components of the rolling texture. This occurs when the average thickness of the rolled grains and deformation bands is less,³³ i.e. when the penultimate grain-size is smaller or reductions are higher.

V.—CONCLUSIONS

(1) Both sintered and resintered thorium show a (123)[$\bar{1}\bar{2}\bar{1}$] type of deformation texture on rolling.

(2) The normal compression texture associated with this type of rolling texture, i.e. strong [110] with a spread to [100] and [311], is also exhibited.

(3) The observed textures can be accounted for on the basis of slip on the octahedral planes in the direction of the face diagonals.

(4) It is suggested that this texture behaviour may be taken to indicate: (a) the absence of any yield phenomena in the face-centred cubic thorium lattice, and (b) the absence of any region of low work-hardening in its stress/strain curve. This in turn leads to the assumption that the slip systems in thorium harden equally.

(5) On annealing, a re-orientation of the structure corresponding to a 30° – 40° rotation takes place, to give the cube texture (100)[001].

(6) This annealing behaviour can be explained on the basis of high grain-boundary mobility.³⁴ Thus a high-angle boundary (30° – 40° rotation) may be thought of as a continuous (monatomic) layer of disordered atoms, such that each atom in the boundary is near to an irregularity analogous to a vacant site, so that atomic migration in the boundary layer is rapid.

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REFERENCES

1. P. Chiotti, *J. Electrochem. Soc.*, 1954, **101**, 567.
2. C. S. Barrett, "The Structure of Metals", 2nd edn. 1953 : New York and London (McGraw-Hill).
3. R. M. Brick, "Cold Working of Metals", p. 99. 1949 : Cleveland (Amer. Soc. Metals).
4. T. Ll. Richards, "Progress in Metal Physics", Vol. I, p. 281. 1949 : London (Butterworths Scientific Publications).
5. G. Sachs and J. Spretnak, *Trans. Amer. Inst. Min. Met. Eng.*, 1940, **140**, 359.
6. O. Dahl and F. Pawlek, *Z. Metallkunde*, 1936, **28**, 266.
7. C. S. Barrett and F. W. Steadman, *Trans. Amer. Inst. Min. Met. Eng.*, 1942, **147**, 57.
8. H. Hu and P. A. Beck, *J. Metals*, 1950, **2**, 1214.
9. C. G. Dunn, "Cold Working of Metals", p. 113. 1949 : Cleveland (Amer. Soc. Metals).
10. A. Winogradski, *Rev. Mét.*, 1954, **51**, 597.
11. J. Adam and J. Stephenson, *J. Inst. Metals*, 1953-54, **82**, (12), 561.
12. J. F. H. Custers, *Physica*, 1948, **14**, 453.
13. J. Thewlis and A. R. Pollock, *J. Sci. Instruments*, 1950, **27**, 72.
14. L. G. Schulz, *J. Appl. Physics*, 1949, **20**, 1033.
15. G. B. Harris, *Phil. Mag.*, 1952, [vii], **43**, 113.
16. C. S. Barrett, "The Structure of Metals", 2nd edn., p. 181. 1953 : New York and London (McGraw-Hill).
17. F. Wever, *Trans. Amer. Inst. Min. Met. Eng., Inst. Metals Div.*, 1931, 51.
18. H. Hu, P. R. Sperry, and P. A. Beck, *ibid.*, 1952, **194**, 76.
19. G. I. Taylor, *J. Inst. Metals*, 1938, **62**, 307.
20. E. A. Calnan and C. J. B. Clews, *Phil. Mag.*, 1950, [vii], **41**, 1085.
21. A. H. Cottrell, "Dislocations and Plastic Flow in Crystals". 1953 : Oxford (Clarendon Press).
22. C. F. Elam, *Proc. Roy. Soc.*, 1936, [A], **153**, 273.
23. E. A. Calnan, *Acta Met.*, 1954, **2**, 865.
24. A. H. Cottrell, "Relation of Properties to Microstructure", p. 131. 1954 : Cleveland (Amer. Soc. Metals).
25. R. E. Smallman, G. K. Williamson, and G. Ardley, *Acta Met.*, 1953, **1**, 126.
26. P. A. Beck and H. Hu, *Trans. Amer. Inst. Min. Met. Eng.*, 1952, **194**, 83.
27. R. M. Brick, D. L. Martin, and R. P. Angier, *Trans. Amer. Soc. Metals*, 1943, **31**, 675.
28. W. R. Hibbard and D. E. Trout, *Trans. Amer. Inst. Min. Met. Eng.*, 1949, **185**, 620.
29. C. S. Barrett, *ibid.*, 1940, **137**, 128.
30. P. A. Beck, W. G. Burgers, and T. J. Tiedema, *Acta Met.*, 1953, **1**, 230.
31. P. A. Beck, *Trans. Amer. Inst. Min. Met. Eng.*, 1951, **191**, 474.
32. W. H. Baldwin, *ibid.*, 1946, **166**, 591.
33. M. Cook and T. Ll. Richards, *J. Inst. Metals*, 1943, **69**, 351.
34. M. L. Kronberg and F. H. Wilson, *Trans. Amer. Inst. Min. Met. Eng.*, 1949, **185**, 501.

A PRELIMINARY NOTE ON THE CREEP PROPERTIES OF INTERNALLY OXIDIZED COPPER ALLOYS*

1614

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SYNOPSIS

Polycrystalline and single-crystal specimens of copper containing dispersed non-metallic phases were prepared by the technique of internal oxidation, and 100-hr. constant-load creep tests were carried out at 200° C. A considerable improvement in creep-resistance under a stress of 3 tons/in.² was found on internally oxidizing a polycrystalline copper-0.05% aluminium alloy at 900° and 850° C.

The creep-resistance of internally oxidized single crystals of a copper-0.3% silicon alloy was found to depend on the degree of dispersion of the oxide, the greater creep-resistance being shown by specimens containing the finer dispersion.

I.—INTRODUCTION

THE technique of internal oxidation has been employed to produce a dispersed non-metallic phase in copper. An alloy suitable for this treatment consists of a dilute solid solution of a base metal in a more noble metal. The alloy is heated under oxidizing conditions, so that oxygen diffuses into the alloy and produces a dispersion of the oxide of the base metal in a matrix of the noble metal.

The creep-resistance of some internally oxidized polycrystalline materials has been studied by de Jong.¹ He worked with beryllium-bearing copper alloys, and noted the effect of a shallow layer of subscale on the creep properties of the alloy. He stressed the importance of the stability of the dispersed phase at high temperatures as a factor in determining creep-resistance.

The present work was carried out with a Chevenard² creep machine. The creep properties of single-crystal and polycrystalline specimens were determined with, and without, a dispersed oxide phase.

II.—EXPERIMENTAL

1. PREPARATION OF SPECIMENS

The specimens were 4 mm. in dia. with 32 mm. between the threaded ends, the parallel test section and fillets being "plunge" ground with a profiled emery wheel.

Single crystals of pure copper and copper-0.3% silicon alloy were grown by the Bridgman technique. The alloy crystals were internally oxidized before machining. In every case machining was carried out with great care to avoid distortion of the specimen.

2. METHOD

Reference to some of the literature concerning the creep properties of copper^{3,4} revealed that many of the data referred to a testing temperature of 200° C. Accordingly, this temperature was selected for carrying out the present tests.

Short tests, of the order of 100 hr., were performed, in order to reveal any general differences in behaviour between the various materials tested. Only the time-dependent elongation was plotted, the initial extension on adding the load being disregarded.

With reference to the present creep curves it must be emphasized that only a comparison of creep *rates* can be made with accuracy, owing to the uncertainty in assessing the initial parts of the curves as plotted by the Chevenard machine. The maximum rate of "follow-up" by the servo-motor of the extensometer mechanism corresponds to an extension rate of 0.00074 cm./min., and so a higher initial rate of extension is not recorded, since it becomes indistinguishable from the initial extension on applying the load.

After the specimen had been inserted into the machine, the furnace was switched on and the temperature of the specimen adjusted to a uniform and constant value. The specimen was maintained in the unloaded condition at 200° C. for several hours, to relieve any stresses introduced by the machining operation.

3. TESTS ON POLYCRYSTALLINE MATERIAL

(a) *Effect of a Dispersion*

Experiments were carried out to compare the creep behaviour of pure copper with that of an internally oxidized specimen of similar grain-size. With speci-

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900° C. The microstructure of the heat-treated material did not appear to be significantly different from that observed in the as-oxidized material (Fig. 4, Plate LXIII).

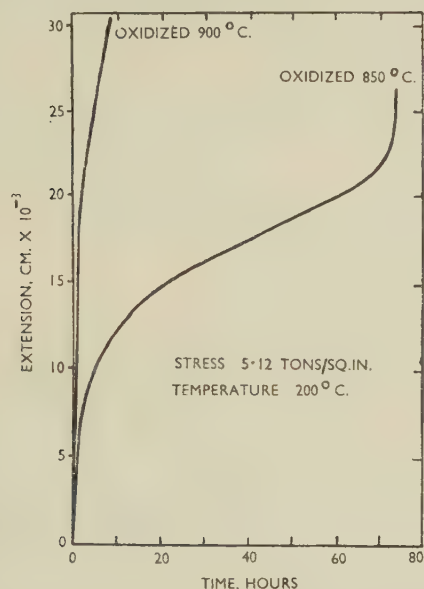


FIG. 2.—Creep Curves of Internally Oxidized Polycrystalline Copper-0.05% Aluminium Alloy.

4. TESTS ON SINGLE-CRYSTAL SPECIMENS

In spite of the longer time needed for the oxidation of silicon-bearing alloys, they were employed for the production of single crystals, since a suitable refractory was not available to contain the aluminium-bearing alloy.

(a) *Copper-0.3% Silicon Alloy, Unoxidized*

A test on an unoxidized single crystal at 200° C. resulted in no creep. Stresses of up to 6 tons/in.² in steps of 0.5 ton/in.² were applied to the specimen for 30 hr., and in every case the specimen behaved in the same way. An instantaneous extension took place within the first few minutes of applying the load, and subsequently no creep was recorded. The total extension was approximately 14%. It appeared that viscous creep (often associated with grain-boundary movement in polycrystalline specimens) was entirely absent, only a rapid initial extension taking place.

To confirm this interpretation, the specimen was annealed at 1000° C. for 1 hr. to induce recrystallization. The resulting microstructure was coarsely polycrystalline, with a grain-size of 2-3 mm. The specimen was then retested at a stress of approximately 2 tons/in.². This treatment, which resulted in the formation of grain boundaries in the structure, also gave rise to creep.

(b) *Copper-0.3% Silicon Alloy, Oxidized at 900° C.*

The specimens were internally oxidized by packing in a copper powder/cuprous oxide mixture, and

heating at 900° C. for 8 weeks. The resulting microstructure is shown in Fig. 5 (Plate LXIII).

The creep curve for this material, under a stress of 5.12 tons/in.² at 200° C., is shown in Fig. 3, and its behaviour may be compared with that of an unoxidized polycrystalline specimen annealed at 1000° C. (grain dia. approx. 1 mm.). The considerable "instantaneous" plastic flow which took place on applying the load was not recorded. Another specimen tested at 3.1 tons/in.² did not creep.

(c) *Copper-0.3% Silicon Alloy, Oxidized at 1000° C.*

The specimens were internally oxidized at 1000° C. for 16 days, to produce a fully oxidized cross-section. The creep curve for this material, tested under similar conditions to (b) above, also appears in Fig. 3. The creep rate was higher than that of the specimen containing the finer dispersion, in (b) above. Again, no creep was recorded at a stress of 3.1 tons/in.².

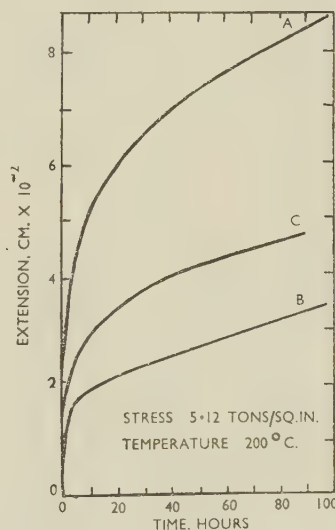


FIG. 3.—Creep Curves of Copper-0.3% Silicon Alloy.

KEY.

- A. Single crystal, oxidized at 1000° C.
B. " " " 900° C.
C. Polycrystalline, vacuum-annealed at 1000° C.

5. PARTICLE-SIZE ESTIMATION

The oxide particles were extracted by dissolving the metal and subsequent dialysis. A drop of the resulting suspension was placed on an electron-microscope copper grid bearing a collodion film. When dry, this was examined in an electron microscope, and the particles photographed and measured. Their mean sizes were estimated to be :

- (i) Cu-0.05% Al oxidized at 850° C. and 900° C.—500 Å.
- (ii) Cu-0.3% Si oxidized at 900° C.—3000 Å.
- (iii) Cu-0.3% Si oxidized at 1000° C.—6000 Å.

III.—DISCUSSION OF RESULTS

1. TESTS ON POLYCRYSTALLINE MATERIAL

Mott,⁵ who has recently discussed transient and steady-state creep from a theoretical standpoint, considers that the ideal creep-resistant material would be one of fine grain-size in which the grain boundaries were filled with oxide, or carbide, or some substance adhering with sufficient strength to the grain for the grain-boundary diffusion of dislocations to be small. Mott suggests that the high creep-resistance of "S.A.P." described by Irmann⁶ is due to this effect.

Although the materials tested above were not of particularly fine grain-size, the grain-boundary precipitate clearly played an important part in contributing to the high creep-resistance observed. From a comparison of curves *B* and *D* (Fig. 1) it is clear that the presence of the particles outweighed the effect of the grain boundaries on the creep properties. Although the specimen oxidized at 850° C. had a finer grain-size than that oxidized at 900° C., the former showed a slightly better creep-resistance.

A similar result was reported by Davis and Thompson⁷ in their investigation of creep in a precipitation-hardened copper-2.75% silver alloy. The effect of grain boundaries on the observed phenomena was found to be negligible compared with that of the precipitate.

With regard to the effect of the high-temperature anneal on the creep rates of these specimens, heating the disperse phase above the temperature at which it was formed results in no marked growth of the particles. However, there may be a tendency for grain-boundary coarsening of particles to occur under these conditions, and such a change could lead to the increased creep rate observed after the reheating. The greater the "degree of superheat" (i.e. the temperature of anneal in excess of the oxidation temperature), the more likely it is that such coarsening will occur. This would explain the fact that the specimen oxidized at 850° C. had a greater creep rate after annealing at 1000° C.

2. TESTS ON SINGLE CRYSTALS

(a) *Unoxidized*

The results for this material indicate that, under the conditions of stress and temperature employed, the observed creep in polycrystalline annealed specimens was associated with grain-boundary movement. As soon as grain boundaries were introduced into the specimen, creep was observed.

(b) *Internally Oxidized*

In one respect, particles produced the same effect as grain boundaries, in that creep was observed when they were present. Higher stresses were required, however, to bring about this creep, for no specimen oxidized at 900° or 1000° C. showed any creep under a stress of 3.1 tons/in.².

The effect of particle size on the creep properties was such that the specimen containing the finer dispersion had the lower creep rate. This general effect was also observed in the polycrystalline specimens containing the alumina dispersions, although the average particle size was considerably smaller in this case.

IV.—CONCLUSIONS

(1) A considerable improvement in creep-resistance at 200° C. took place on internally oxidizing polycrystalline copper-0.05% aluminium alloy at 900° and 850° C. The lower the temperature of oxidation, the greater was the creep-resistance of the resulting material. These results apply to stresses of 3.1 tons/in.²; when the stress was raised to 5.12 tons/in.², rapid creep occurred, and intergranular failure took place early in the test.

(2) At 200° C., an annealed single crystal of copper-0.3% silicon alloy underwent considerable plastic flow on applying the load, but stresses up to 6 tons/in.² produced no subsequent creep. On recrystallizing the specimen, creep took place immediately.

(3) The creep-resistance of internally oxidized single crystals of copper-0.3% silicon alloy depended on the degree of dispersion of the oxide. The creep-resistance increased as the temperature of oxidation decreased, i.e. as the dispersion became finer.

ACKNOWLEDGEMENTS

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REFERENCES

1. J. J. de Jong, *Ingenieur*, 1952, **64**, (28), O.92.
2. P. Chevenard, *Rev. Mét.*, 1942, **39**, 321, 353.
3. E. R. Parker, *Trans. Amer. Soc. Metals*, 1941, **29**, 269.
4. E. R. Parker and C. Ferguson, *ibid.*, 1943, **31**, 699.
5. N. F. Mott, *Phil. Mag.*, 1953, [vii], **44**, 742.
6. R. Irmann, *Rev. Aluminium*, 1951, (179), 268.
7. M. Davis and N. Thompson, *Proc. Phys. Soc.*, 1950, [B], **63**, 847.

THE SINTERING, FABRICATION, AND PROPERTIES OF THORIUM*

1615

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SYNOPSIS

The powder metallurgy of thorium has been studied over a range of compacting pressures and sintering temperatures. The optimum conditions were obtained by pressing at 22.5 tons/in.², and then sintering in high vacuum for 2 hr. at 1300° C. Metal of density approaching the theoretical was obtained by resintering after cold rolling to 50% reduction of thickness. Resintered metal, though having an average oxide content of 1.75 wt.-%, was still very ductile.

The influence of cold rolling on the mechanical properties of thorium has been determined, and the recovery and recrystallization of the cold-worked metal on subsequent annealing has been investigated for a range of deformations and temperatures.

I.—INTRODUCTION

THORIUM metal has been prepared in powder form since the middle of last century, and by 1927 Marden and Rentschler¹ had developed a workable commercial process, based on the reduction of thorium by calcium, for producing pure powder in quantity. In contrast, little work has been published on the consolidation of thorium powder, and on the properties of the consolidated metal. Several workers, notably Davenport² and Thompson,³ encountered great difficulty in melting thorium, because of its reactivity, and it is not surprising to find that most effort has been in the field of powder-metallurgical techniques.⁴⁻⁶ Marden⁶ produced workable thorium by sintering at 800° C., but more recent commercial practice utilizes a compacting pressure of 19 tons/in.² and a sintering temperature⁵ between 1327° and 1357° C. Davenport² pressed the powder at 33 tons/in.², and subsequently sintered it at 1175° C. to give metal with a density of 10.7 g./c.c. The mechanical properties reported are unlikely to be typical of fully consolidated thorium, which has a density of 11.7 g./c.c., according to van Arkel.⁷

The main impurity in the sintered metal is oxygen, present as discrete particles of thorium dioxide.² In the earlier work, oxide contents of 3–4 wt.-% were common, but the metal was very ductile.⁸⁻¹¹ Small concentrations of iron,^{1,5} silicon,¹ calcium,⁵ and carbon² tend to embrittle the metal.

The present paper provides systematic data on the sintering and working of relatively pure thorium as the first steps in a programme of work on the properties of thorium-base alloys.

II.—EXPERIMENTAL METHODS

1. RAW MATERIAL

The thorium powder had been carefully prepared to avoid undue oxygen contamination, and had been

sieved to –200 mesh when received. Its oxide content was not greater than 0.4 wt.-%, and was possibly much less. The uncertainty is due to the fact that accurate oxygen analyses were possible only on sintered metal. The main metallic impurities were calcium (300 p.p.m.), magnesium (160 p.p.m.), and iron (47 p.p.m.).

2. COMPACTING TECHNIQUE

The die used consisted of two heavy steel plates bolted together through spacers at each end to form a cavity with a cross-section of 5 × 50 mm., and sufficiently deep (40 mm.) to guide the upper and lower punches. The whole assembly was used on the compression beam of a testing machine to give compacts 5 × 5 × 50 mm.

Powder was compacted with the die “floating”,¹² to minimize the effects of die-wall friction without the risk of contamination from a lubricant. The powder had a marked tendency to seize to the die walls under pressure, and cracks frequently formed when compacts were ejected. The compacts were therefore removed by dismantling the die.

3. SINTERING AND ANNEALING

Both sintering and annealing were carried out in a horizontal platinum-wound furnace having a mullite tube, under a vacuum of 3×10^{-5} – 5×10^{-5} mm. of mercury at temperature. Specimens were supported by a grid of molybdenum wire held in a molybdenum boat, which could be moved in and out of the hot zone at will by means of a stainless-steel rod, working through a Wilson seal. Temperatures were measured by means of a platinum/platinum-rhodium thermocouple with its hot junction immediately beneath the boat.

4. DENSITY MEASUREMENT

Preliminary work showed that the use of water for determining the bulk volume of compacts did not give

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reliable values, owing to seepage into the open pores. There was no such error with mercury, and densities reported below were determined from the force required to hold a weighed specimen just under mercury.¹³ Densities determined in this way agreed closely with those obtained from the dimensions of the specimens, and could be determined to ± 0.01 g./c.c.

5. ELECTRICAL RESISTIVITY

Resistivity was used to give a general indication of the purity of sintered bars in relation to sintering conditions. Bars with a uniform cross-section were always used, and surface oxide was removed by emery paper.

6. MECHANICAL PROPERTIES

Tensile specimens were stamped from cold-rolled strip after various amounts of deformation. The specimens were $2\frac{3}{4}$ in. long, with a gauge-length of 1 in. \times 0.124–0.125 in., the thickness depending on the degree of deformation. Hardness measurements were made on the shoulders, before testing. In the case of as-sintered bars, the specimens were prepared by turning.

7. METALLOGRAPHY

Specimens for microscopic examination were prepared by rubbing down on a series of emery papers lubricated with white spirit, followed by polishing on a damp pad impregnated with 500-grade carborundum. The final polishing was carried out with diamond dust ($0.1\ \mu$), to give clear definition of the oxide inclusions and pores. The matrix, however, showed fine scratches, which could be eliminated, if need be, by lightly polishing with the finest grade alumina paste.

Specimens were also electrolytically polished in an electrolyte containing 70 c.c. glacial acetic acid, 20 c.c. perchloric acid (sp. gr. 1.64), and 5 c.c. water, at about 10°C ., using a current density of 0.6 amp./cm.². Specimens were taken at the rough-polished stage and electropolished for 7–12 sec. Longer times were required for grain-boundary etching, which occurred at the expense of severe pitting in the vicinity of oxide inclusions and pores.

Satisfactory etching reagents were difficult to find, the best results being obtained electrolytically, using a solution consisting of 50 c.c. orthophosphoric acid and 50 c.c. glacial acetic acid.¹⁴

With electropolished specimens, both electrolytes gave a grain-contrast etch at a current density of 0.1 amp./cm.² after 30–45 sec. Mechanically polished specimens appeared to develop a uniform oxide film, which subsequently cracked to give markings resembling grain boundaries. For reliable etching, the deformed surface layer had to be removed.

8. GRAIN-SIZE MEASUREMENT

Grain-size was determined by counting the number of grains intercepted by a line, 10 cm. long, drawn on the screen of a Vickers projection microscope. Two counts were made at right angles on each field, and, provided that the magnification was arranged to give more than 20 intercepts, counts on 6 random fields were sufficient to give results with an error of $\pm 5\%$.

III.—EXPERIMENTAL RESULTS

1. SINTERING DATA

(a) Optimum Compacting Pressure

With a reactive metal like thorium, air adsorbed on the powder or trapped during compacting gives rise

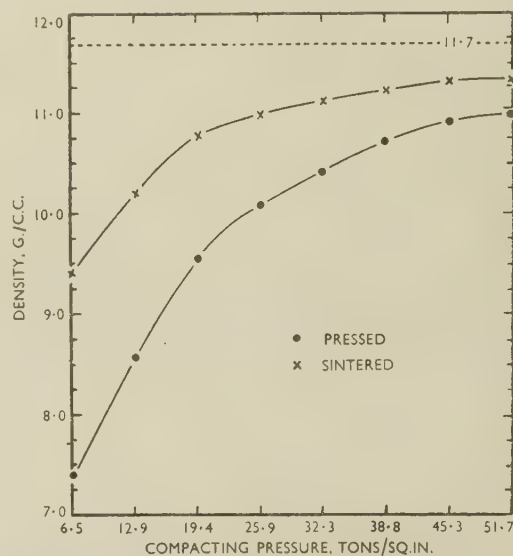


Fig. 1.—The Influence of Compacting Pressure on the Density of Thorium Compacts in the Pressed Condition, and After Sintering for 3 Hr. at 1200°C .

to contamination during sintering if it is not allowed to escape. The first experiments were therefore made with the object of determining a suitable pressure to give compacts with adequate green strength, yet with interconnected pores.

Compacts formed at pressures varying from 6.45 to 51.7 tons/in.², had the green densities plotted in Fig. 1. There is a marked change in the slope of the curve over the range 19.4–25.9 tons/in.², which indicates, according to Seelig and Wulff,¹⁵ that plastic deformation of the powder particles is taking place at higher pressures, and thus the channels between particles are closed up. The compacts were sintered for 3 hr. at 1200°C ., and the sintered densities are also plotted in Fig. 1. It should be noted that compacting pressures over 25.7 tons/in.² have only a small effect on sintered density. The

electrical resistivity of the sintered compacts (Fig. 2) shows a well-defined minimum at 25.9 tons/in.²; above this pressure, the resistivity increases with

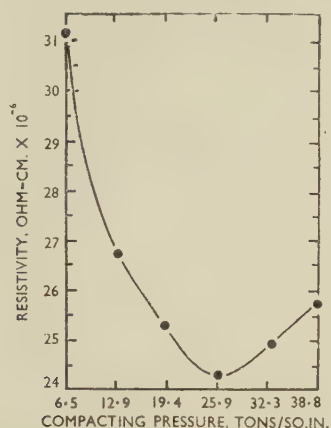


FIG. 2.—Effect of Compacting Pressure on the Resistivity of Thorium Compacts Sintered for 3 Hr. at 1200° C.

compacting pressure, although the sintered density is also increasing (Fig. 1). This behaviour is attributed to increased contamination caused by air which has been unable to escape from the compacts pressed at the higher pressures.

The above results led to the choice of a compacting pressure of 22.5 tons/in.², to minimize contamination. All bars used in the investigation of other sintering variables, and of mechanical properties, were compacted at this pressure.

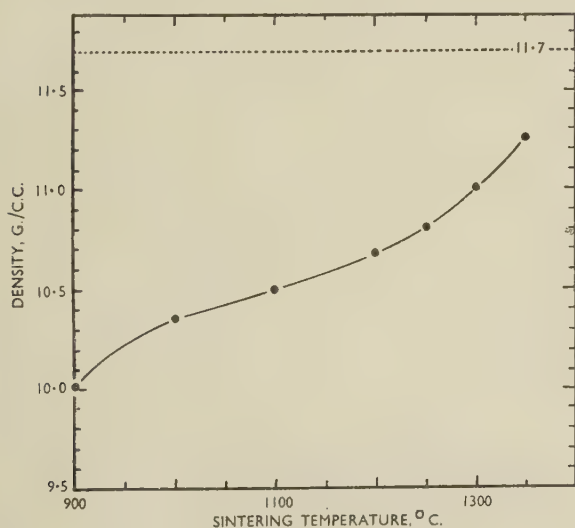


FIG. 3.—Effect of Sintering Temperature on the Density of Thorium Compacts Pressed at 22.5 tons/in.² and Sintered for 2 Hr.

(b) Sintering Temperature

Compacts pressed at 22.5 tons/in.² were sintered for 2 hr. at temperatures in the range 900°–1350° C. Some degree of sintering occurred even at the lowest

temperatures, but above 1200° C. the rate increased rapidly, as shown by the density measurements (Fig. 3). High temperatures (above 1300° C.) undoubtedly gave compacts of high density, but electrical-resistivity measurements indicated that contamination took place in the range 1300°–1350° C., particularly in cases when the vacuum was poorer than usual. Extensive alloying with the molybdenum boat prevented the use of higher temperatures, and in fact alloying was noticeable at points of contact at all temperatures above 1300° C. On this evidence, 1300° C. was chosen as the optimum sintering temperature and was used in all subsequent work.

(c) Sintering Time

Bars pressed at 22.5 tons/in.² were sintered at 1300° C. for times varying from $\frac{1}{2}$ to 8 hr. The results, plotted in Fig. 4, indicate that the greatest change in

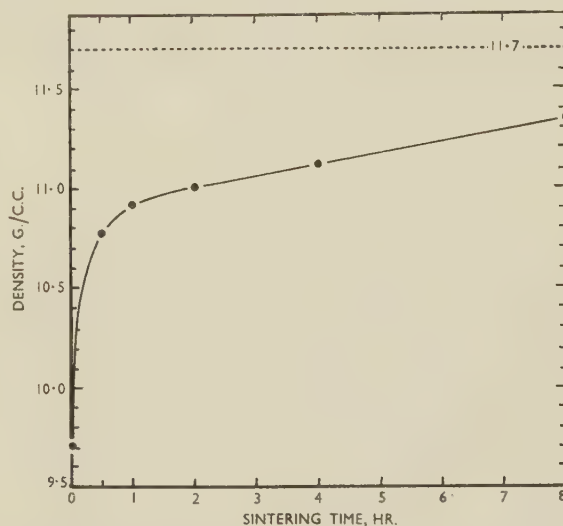


FIG. 4.—Density of Thorium Compacts Pressed at 22.5 tons/in.² and Sintered at 1300° C., in Relation to Sintering Time.

density occurred within the first 2 hr. Very prolonged heating would obviously be necessary to approach the theoretical density; this led to a study of the effects of resintering after cold working.

(d) Resintering

The optimum sintering treatment chosen as a result of the above experiments was to press the bars at 22.5 tons/in.², and sinter for 2 hr. at 1300° C. to give sintered metal with a density of 11.0–11.1 g./c.c. This material was readily cold rolled to half thickness (see below). This treatment, followed by resintering for 1–2 hr. at 1300° C., resulted in metal with a density of 11.60–11.65 g./c.c., as compared with a theoretical value of 11.67 g./c.c. (allowing for the presence of 2% oxide). Unless otherwise stated, all mechanical properties reported in this paper have been determined on resintered metal.

(e) *Microstructure*

A typical unetched section of sintered thorium, polished with diamond dust, is shown in Fig. 5 (Plate LXIII). Thoria appears as well-defined inclusions, which were first observed by Davenport²; the particles have a characteristic blue-grey colour in white light. Porosity appears as dark, irregular regions in Fig. 5. Estimation of the relative proportions of thorium and thoria by point-counting on unetched sections gave values between 1 and 2 wt.-% of oxide, which were in good agreement with values determined by vacuum fusion, e.g. 1.65 and 1.15, compared with 1.62 and 1.20 respectively.

Variable amounts of a hard white phase were a usual feature of unetched sections. Davenport, who observed a similar constituent, suggested it was a carbide, but examination of compacts sintered with deliberate additions has led the present authors to attribute it to the presence of iron, probably originating from the die. Electrolytic etching also caused the phase to stand out brilliantly white, as shown in Fig. 6 (Plate LXIII). A typical microstructure of the etched metal is shown in Fig. 7 (Plate LXIII).

2. WORKING AND ANNEALING

(a) *Working*

In confirmation of reports of high ductility by earlier workers, both the sintered and resintered metal possessed very satisfactory cold-working properties. Sintered metal could be cold rolled to 70% reduction in thickness without intermediate annealing before edge-cracking occurred; resintered metal could be rolled beyond a reduction of 95% without annealing, showing no sign of cracking. It was essential to ensure adequate lubrication during rolling to counteract the tendency of thorium under pressure to weld or stick to steel.

Similar cold reductions could be obtained by hammering, though this was a much less satisfactory means of working because of a tendency for the metal to fail by the formation of longitudinal cracks. Some attempts were made to draw thorium, but in the majority of cases the wire broke. It had a rough, cracked surface, indicating considerable friction between die and wire, and it appeared that this was the cause of failure, rather than the low tensile strength of the metal, which was the view held by Marden and Rentschler.¹ This method of fabrication should be possible if a suitable lubricant can be found.

(b) *Mechanical Properties*

The mechanical properties obtained on resintered and cold-worked metal are shown in Fig. 8, and, for two typical samples of sintered metal, values were:

Max Stress, tons/in. ²	Elongation, %	Reduction in Area, %	Vickers Hard- ness No.
16.4	18	14	71.6
15.0	40	35	74.1

Results from sintered thorium varied from sample to sample, but much more consistent values were

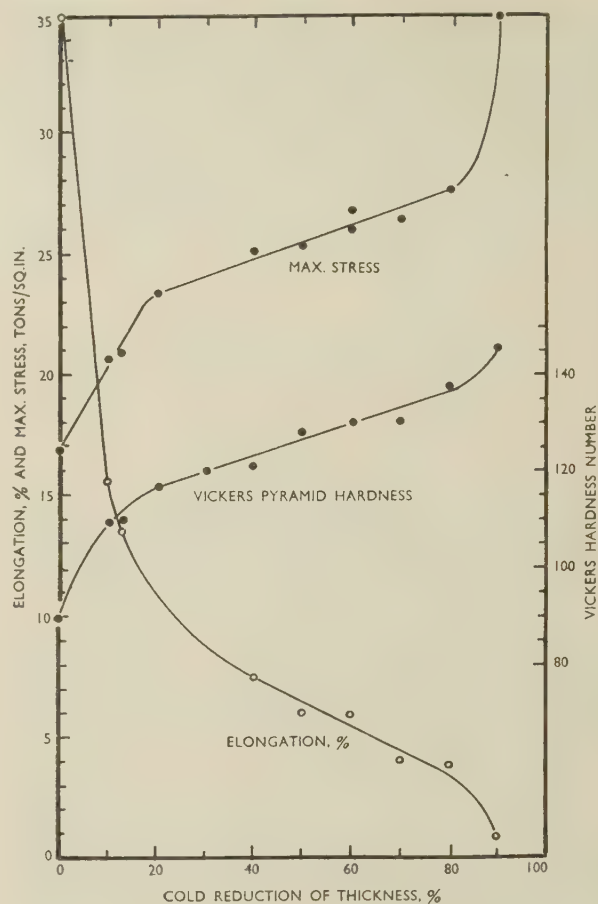


FIG. 8.—Mechanical Properties of Resintered Thorium in the Annealed and Cold-Worked Condition.

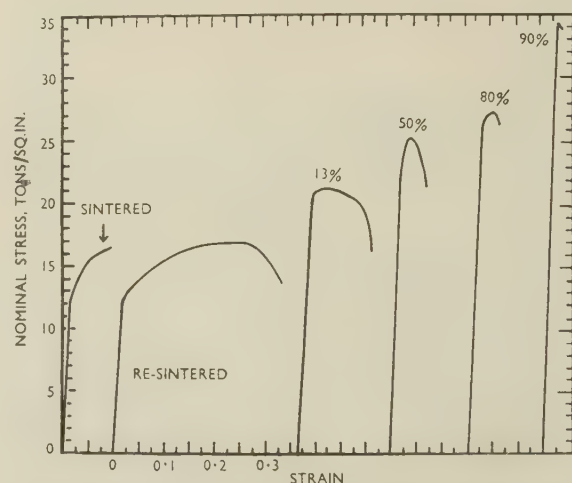


FIG. 9.—Influence of Cold Work on the Stress/Strain Curves of Resintered Thorium. The percentages refer to reduction of thickness.

obtained on resintered metal. The maximum stress values determined in the present work are in general agreement with those obtained by Davenport² (17.1 tons/in.² sintered; 38.3 tons/in.² after heavy

cold work), but in all cases the ductility values are much higher.

The rate of work-hardening (Fig. 8) is particularly rapid over the first 10% of deformation, behaviour which is reflected in the marked shortening of the plastic range of the stress/strain curves of metal rolled beyond this stage (Fig. 9).

(c) Annealing of Cold-Worked Thorium

Specimens from thorium strip, cold rolled to 30, 70, and 90% reduction in thickness, were annealed between 100° and 1300° C. for $\frac{1}{2}$ hr. Hardness measurements (Fig. 10) showed that softening was complete in the range 700°–750° C., having begun some 250° C. below.

At all deformations, the fully recrystallized grain structure appeared when softening was complete.

TABLE I.—Grain-Size (Grains/mm.) of Thorium Annealed after Reductions in Thickness of 30, 70, and 90%.

Annealing Time, min.	Annealed at 750° C.			Annealed at 1208° C.		
	30%	70%	90%	30%	70%	90%
5	38.1	39.9	33.6
15	62	104	136	31.2	32.1	33.3
30	53.7	84.1	112	29.3	28.9	33.9
60	55	77.9	97.5	29.1	29.7	30.0
120	49.5	65	95.4	28.8	28.6	27.9

In the region of 700° C., there was a marked dependence of recrystallized grain-size on deformation, which persisted after prolonged annealing (Table I). At higher temperatures (Table I), grain growth took

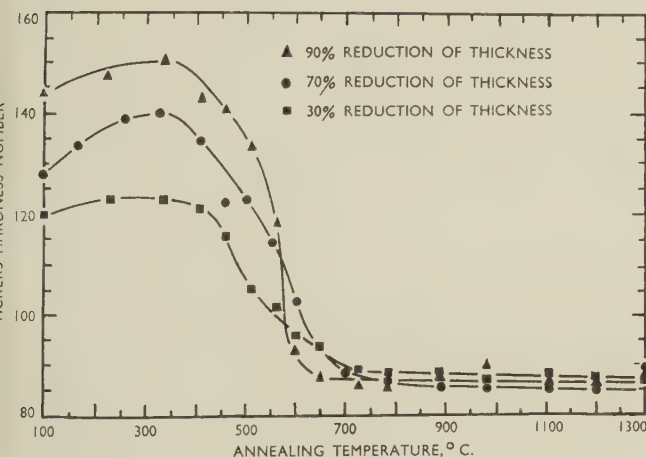


FIG. 10.—Effect of Annealing for 30 Min. on the Hardness of Cold-Rolled Thorium.

place rapidly, and differences due to deformation soon disappeared. Fig. 11 also shows this tendency clearly.

The appreciable rise in hardness on annealing at low temperatures (100°–350° C.) (Fig. 10) suggests that some non-metallic impurity is giving rise to strain-ageing or a related phenomenon. This effect is receiving further attention.

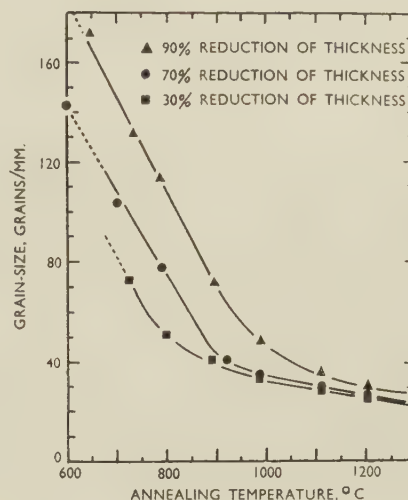


FIG. 11.—Effect of Annealing for 30 Min. on the Recrystallized Grain-Size of Cold-Rolled Thorium. Where dotted, the curves indicate partial recrystallization.

IV.—DISCUSSION AND CONCLUSIONS

It has been shown that thorium powder may be readily sintered and fabricated to produce metal of high density, with an oxide content between 1.5 and 2.0 wt.-%. The optimum conditions appear to be pressing at approximately 22 tons/in.², followed by sintering for 2 hr. at 1300° C. This treatment results in a density of about 11.0 g./c.c., which can be raised to 11.60–11.65 g./c.c. by cold rolling to 50% reduction of thickness, followed by resintering for 1–2 hr. at 1300° C.

The main impurity in sintered thorium is oxygen, present as a microscopic dispersion of thoria particles. The percentage of thoria present can be reliably determined by point-counting. Somewhat surprisingly, the oxide does not prevent the metal's being very ductile and readily cold worked. It is hoped later to present data on metal containing different percentages of oxide.

The good working characteristics of the metal are in accordance with the known properties of other face-centred cubic metals. Oxygen appears to have a more marked effect on metals with non-cubic structures, e.g. titanium and zirconium. The earlier work on thorium has thus been substantiated, but it should be emphasized that the metal used in the present investigation yielded even more satisfactory properties, presumably because of its higher purity.

Rolling is a very feasible method of fabrication, but other methods, such as wire-drawing, may present a problem in lubrication. This is also an

important factor in the pressing of thorium powder, where a lubricant is required, though it can be used only at the risk of contaminating the sintered metal. Similar considerations may well apply to other forming and shaping operations.

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REFERENCES

1. J. W. Marden and H. C. Rentschler, *Indust. and Eng. Chem.*, 1927, **19**, 97.
2. E. S. Davenport, *Trans. Amer. Inst. Min. Met. Eng., Inst. Metals Div.*, 1930, 538.
3. J. G. Thompson, *Metals and Alloys*, 1933, **4**, 114.
4. W. Kroll, *Z. Metallkunde*, 1936, **28**, 30.
D. Bender, *ibid.*, 1949, **40**, 257.
5. —, *Brit. Intelligence Objectives Sub-Committee, Final Rep.* No. 276, Item No. 7 (1946).
6. J. W. Marden, *Trans. Electrochem. Soc.*, 1934, **66**, 39.
7. A. E. van Arkel, "Reine Metalle", p. 217. 1939: Berlin (Julius Springer).
8. W. von Bolton, *Z. Electrochem.*, 1908, **14**, 768.
9. D. Lely and L. Hamburger, *Z. anorg. Chem.*, 1914, **87**, 209.
10. F. H. Driggs and W. C. Lilliendahl, *Indust. and Eng. Chem.*, 1930, **22**, 1302.
11. R. Kieffer and W. Hotop, "Pulvermetallurgie und Sinterwerkstoffe", p. 176. 1943: Berlin (Julius Springer).
12. C. G. Goetzel, "Treatise on Powder Metallurgy", Vol. I, p. 349. 1949: New York (Interscience Publishers Inc.); London (Interscience Publishers Ltd.).
13. P. W. Clark and J. White, *Trans. Brit. Ceram. Soc.*, 1950, **49**, 305.
14. H. E. Wilhelm and P. Chiotti, *U.S. Atomic Energy Commission Publ.*, 1949, (AECD-2718).
15. R. W. Seelig and J. Wulff, *Trans. Amer. Inst. Min. Met. Eng.*, 1946, **166**, 492.

SOME OBSERVATIONS ON THE CREEP OF PRE-STRAINED ALUMINIUM*

1616

By G. R. WILMS,† B.Met.E., M.Eng.Sc., Ph.D.

SYNOPSIS

X-Ray and metallographic observations have been made during the creep of specimens of high-purity aluminium after preliminary deformations to produce initial sub-structures of a known type. The experiments have been carried out under constant tensile loads at different temperatures, and the results compared with those obtained on the annealed material strained under the same conditions of load and temperature.

It has been found that the initial sub-structure grows within the grains until it becomes comparable in size to the equilibrium structure produced during secondary creep of the corresponding annealed specimen. This equilibrium structure appeared to be attained by a two-stage process: the first stage is associated essentially with the removal of lattice distortion and perfection of the elements of the sub-structure, and the second stage with a marked growth of the sub-structure. The creep rate remains approximately constant during the first stage, whilst during the second stage the creep rate increases and continues to increase until it becomes comparable to that of the corresponding annealed specimen. Furthermore, the creep deformation is far more effective in activating the growth of the sub-structure than is the heating alone. Finally, the structural changes produced during the creep deformation of the pre-strained metal tend to resist recrystallization; under low loads at 350° C., however, some observations have been made which do not conform to this general behaviour.

I.—INTRODUCTION

ALTHOUGH prior deformation has long been known to modify the creep behaviour of metals, no systematic investigations have been made of the structural changes produced in a pre-strained metal during creep under constant load.

Previous studies¹⁻⁴ of the structural changes occurring during the creep of aluminium have, in general, been carried out on specimens which were initially in the annealed condition. These investigations were concerned primarily with the breaking down of the original perfect grains into a sub-structure. In this connection, it has been shown how the size of the sub-structure is governed by the conditions of the deformation: the sub-structure becomes coarser as the temperature of deformation is increased or as the creep rate decreases, and, with the creep rate constant at a given temperature, the size tends to an equilibrium value.

In the present investigation, however, the essential difference is that the aluminium was subjected to chosen preliminary deformations, so that the grains were dispersed initially into a sub-structure of a known type. The pre-straining was carried out mainly at room temperature. The object of the paper is to record changes which occur in the structure during subsequent creep deformation under constant tensile load at various temperatures. The main result obtained is that the initial broken-down structure grows within the grains into a coarse sub-structure,

the changes being a consequence of the creep deformation rather than of the heating alone. The sub-structure continues to grow until it becomes comparable in size to the equilibrium structure produced during the secondary or steady-state creep of an annealed specimen, where both specimens are subjected to the same load and temperature. Furthermore, the creep rate of the pre-strained specimen eventually becomes similar to that of the annealed metal. There is also evidence that the final equilibrium structure produced in the pre-strained metal may be attained by a two-stage process.

II.—EXPERIMENTAL PROCEDURE

The material used was aluminium of 99.99% purity, in the form of flat tensile specimens of $1\frac{3}{8}$ in. parallel test length and $\frac{5}{16}$ in. \times $\frac{1}{8}$ in. cross-section. These were annealed to give a standard grain-size of 0.15 mm., and then pre-strained by the amounts referred to in the results for individual specimens. The specimens were next electropolished to remove the surface markings produced by the preliminary straining, and then allowed to extend under a constant tensile load at a constant temperature. The creep extension was interrupted at intervals, and the specimens allowed to cool, so that X-ray and metallographic examinations could be carried out. Back-reflection diffraction patterns were obtained from stationary specimens, using cobalt K_{α} radiation.

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III.—RESULTS

1. CHARACTERISTICS OF THE CREEP CURVES

The creep curves of some typical pre-strained specimens, extended under constant tensile load at 250° and 350° C., are shown in Figs. 1 and 2, respectively. The corresponding creep curve of the annealed specimen, extended under the same test conditions, is included in each figure for comparison.

to increase until it finally becomes comparable to that of the corresponding annealed test specimen.

It is convenient to refer to the creep deformation preceding the onset of increasing creep rate as the first stage. The creep rate during this first stage of creep deformation is approximately constant, but will include, at the present time, the initial diminishing rate. The second stage then refers to the creep deformation during which the creep rate is increasing

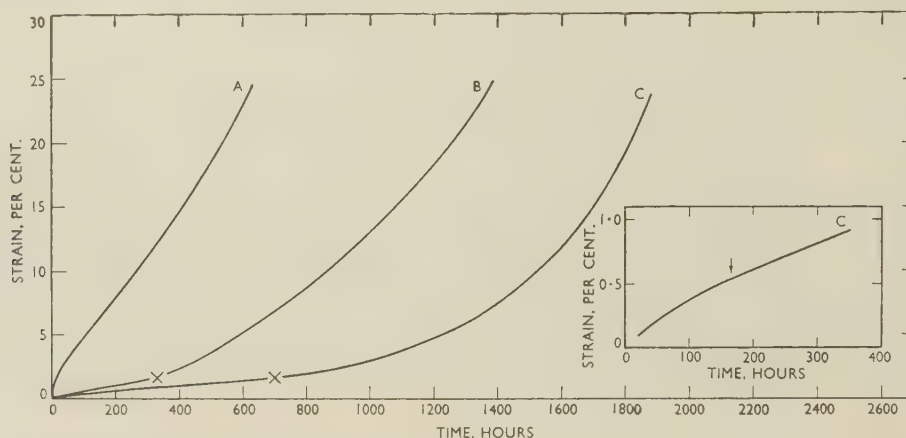


FIG. 1.—Creep of High-Purity Aluminium at 250° C. Under a Constant Load of 700 lb./in.².

Curve A. Annealed specimen.
 „ B. Specimen pre-strained 2.5% at room temperature.
 „ C. „ „ 5% at room temperature.

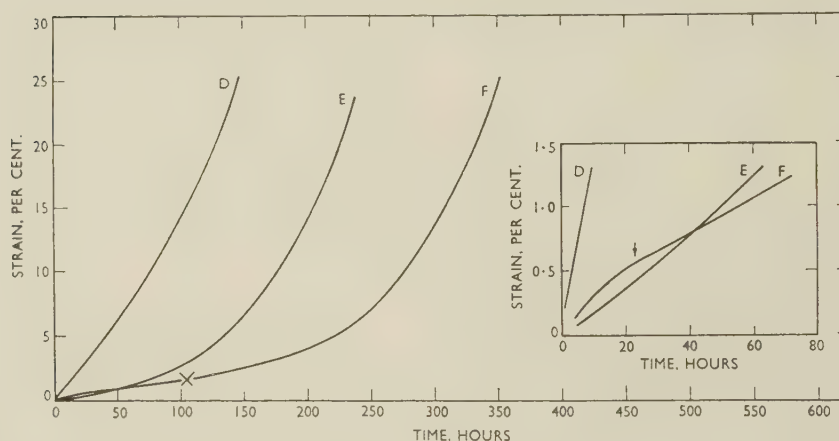


FIG. 2.—Creep of High-Purity Aluminium at 350° C. Under a Constant Load of 250 lb./in.².

Curve D. Annealed specimen.
 „ E. Specimen pre-strained 6.7% at 250° C. under a constant load of 700 lb./in.².
 „ F. „ „ 5.2% at room temperature.

The first feature of the curves for the specimens pre-strained at room temperature is that there is an initial stage of diminishing creep rate (see insets, Figs. 1 and 2). Although this would suggest a stage of transient creep, there is evidence, discussed later, that this is not so. The second feature is that after approximately 0.5% creep extension, marked by arrows on the curves in the inset figures, the creep rate is constant. The third feature is that after 1.7% creep extension, marked by a cross on the respective curves, the creep rate begins to increase, and continues

until it becomes similar to that of the material strained from the initial annealed state under the same conditions of load and temperature.

It will be noted in Fig. 1, that the greater the degree of prior deformation at room temperature, the lower is the creep rate during the first stage, and the time at which the creep rate begins to increase is postponed accordingly. Moreover, the creep rate starts to increase after the same amount of creep extension, namely 1.7%, regardless of the temperature of deformation and the degree of prior deformation.

2. STRUCTURAL CHANGES ASSOCIATED WITH THE CREEP OF PRE-STRAINED ALUMINIUM

The observations refer first to one typical specimen, pre-strained 5% at room temperature, and then extended under a constant load of 700 lb./in.² at 250° C. The prior deformation resulted in a large number of slip lines, which were removed by the electropolishing; a detailed microscopical examination of the specimen after etching revealed traces of slip lines on the surface of some grains, similar to those reported by other workers.⁵ The X-ray examination showed the grains to be considerably broken down, as illustrated by the usual transition from the sharp reflection spots typical of annealed grains (Fig. 7, Plate LXIV) to the apparent continuous arcs typical of deformed grains (Fig. 3, Plate LXIV).

The changes associated with the first stage of the creep deformation are that the original continuous arcs become progressively replaced by discrete reflection spots, as shown in Fig. 4 (Plate LXIV). These changes continue on further deformation until the diffraction pattern consists of a large number of sharp reflection spots distributed around the diffraction rings; at the same time, there is no obvious evidence of the diffuse background associated with the X-ray photographs obtained at the earlier extensions. This is illustrated by Fig. 5 (Plate LXIV), taken after 1.8% extension, which corresponds to a point just after the creep rate had begun to increase. These observations indicate that during the first stage of creep deformation, when the creep rate remains substantially constant, the reflecting elements within the grains are becoming more perfect in structure. Moreover, although the X-ray examination indicates that there is some growth of the sub-structure over this range of extension, it seems significant that the creep rate does remain constant until all evidence of the diffuse background, which arises from the lattice distortion or "disordered material" associated with the initial slip structure, has been removed.

The changes associated with the second stage of the creep deformation are that the reflection spots become progressively less in number and larger in size, until finally no further change is observed on continued extension. The diffraction pattern (Fig. 6, Plate LXIV), is then comparable to that obtained during the secondary or steady-state creep of a specimen strained from the initial annealed state under the same load and temperature. These observations show that during the second stage of creep deformation, when the creep rate is increasing, there is a marked growth of the elements of the sub-structure. The sub-structure finally attains an equilibrium size comparable to that developed in an annealed specimen strained under the same test conditions. At this stage, the creep rates of the pre-strained and annealed specimens are similar (see curves *C* and *A* in Fig. 1).

The corresponding microscopic examination showed that at no stage of the creep deformation were slip lines visible. The changes were similar to those noted

on the corresponding annealed specimen, and were characteristic of the cell structure which has been fully described in earlier papers.^{1,3} A sub-structure could be observed within the grains on careful examination, and this continually increased in size during the deformation. The size of the sub-structure was consistent with that indicated by the X-rays throughout the range of the creep extension.

The same results were obtained on specimens pre-strained by various amounts at room temperature and then extended under the same load at 250° C.

A similar behaviour was observed in tests at 350° C. In this connection, it should first be mentioned that, in accordance with the general relationship between size of sub-structure and temperature of deformation mentioned earlier, an annealed specimen extended at 350° C. can dissociate into a much coarser sub-structure than an equivalent specimen extended at 250° C. For comparison with the results obtained on pre-strained specimens at 250° C., therefore, the observations at 350° C. refer to one typical specimen pre-strained 5.2% at room temperature, and then extended under a constant load of 250 lb./in.². The preliminary structure gave an X-ray pattern similar to that in Fig. 3 (Plate LXIV).

The X-ray photographs, showing the changes during the creep deformation of the pre-strained specimen, are reproduced in Figs. 8–10 (Plate LXIV). The changes associated with the first stage of the creep deformation are similar to those observed at 250° C. The original continuous arcs are again progressively replaced by discrete reflection spots (Fig. 8), so that just after the creep rate begins to increase, the X-ray photograph (Fig. 9) consists of a number of sharp reflection spots with no apparent evidence of the initial diffuse background. However, the alterations in structure for equivalent creep strains appear to be more pronounced at 350° C. than at 250° C. This is clearly shown by a comparison of Fig. 8 with Fig. 4, which illustrates an early stage of the creep extension, and Fig. 9 with Fig. 5, which shows that the sub-structure at the beginning of the second stage is much coarser at 350° C. The principal change associated with the second stage of the creep deformation is a marked growth of the sub-structure, similar to that described previously. The final equilibrium structure (Fig. 10), as indicated by the small number of large reflection spots, is much coarser than that found at 250° C. (Fig. 6). This equilibrium structure, however, is the same as that produced in a specimen extended from the initial annealed state under the same load at 350° C. At this stage, the creep rate of the pre-strained specimen again becomes comparable to that of the annealed specimen, as shown by curves *F* and *D* in Fig. 2. The changes produced during further creep deformation are then similar for both specimens.

The microscopical examination gave no evidence of slip lines during the creep extension; instead, there were marked movements of the grains and of the grain boundaries, similar to those observed on the corre-

sponding annealed specimen. Detailed microscopical examination throughout the range of the creep extension revealed a sub-structure, the size of which was consistent, as before, with that indicated by the X-rays.

It is important to state that at no stage of the creep deformation was the growth of the sub-structures the product of recrystallization, as normally defined. Recrystallization results in the formation of entirely new sets of grains. After repolishing and etching the present specimens, however, the same grains were visible as at the beginning of the test. The observations described relate, therefore, to the building up of the sub-structure within the original grain boundaries.

With reference to the two stages of the creep deformation previously described, the observations indicate that the creep rate does not increase until all evidence of the initial distorted structure has been removed. Therefore, if the preliminary structure is smaller than the characteristic equilibrium size for the temperature and load used, but at the same time shows no evidence of a slip structure, the creep rate should begin to increase soon after the load is applied. Furthermore, an experiment should also prove that the second stage of increasing creep rate is not merely the result of an increase of stress due to the reduction of cross-sectional area. To demonstrate this, a specimen was pre-strained 6.7% under a constant load of 700 lb./in.² at 250° C. The X-ray photograph of the preliminary structure (Fig. 11, Plate LXV) shows a number of sharp reflection spots, with no apparent evidence of the diffuse background which arises from a slip structure. The specimen was then extended under a constant load of 250 lb./in.² at 350° C. On referring to curve *E* in Fig. 2 (see also inset to Fig. 2), it will be observed that the specimen does extend at an increasing rate soon after the load is applied at 350° C. Moreover, this curve can be matched with curve *F*, by transferring the origin of curve *E* to the point marked by a cross on curve *F*. The first stage of the creep deformation has thus been eliminated. During the creep deformation the sub-structure again grows to the size shown in Fig. 12, (Plate LXV), which is the characteristic equilibrium size for the particular temperature and load investigated (Fig. 10, Plate LXIV).

One further point which may be considered here is in regard to the initial stage of decreasing creep rate, observed during the creep deformation of specimens pre-strained at room temperature. As mentioned earlier, this was not considered to be a stage of transient creep for the following reasons. Transient creep is usually regarded as being associated with a strain-hardening process in the metal. For comparable test conditions, therefore, transient creep should become more marked the higher the strain-hardening capacity of the preliminary structure. This would be greatest for the annealed metal, and should progressively diminish as the preliminary structure becomes smaller in size. However, it will be observed in Fig. 2 (more clearly in the inset to the

main figure) that neither the annealed specimen (curve *D*) nor the specimen with the coarse preliminary structure illustrated in Fig. 11 (curve *E*) shows any evidence of a transient stage of creep, whereas the specimen pre-strained at room temperature (curve *F*), which has the finest preliminary structure, does show an initially decreasing creep rate.

Under the conditions of temperature and load considered, the annealed metal dissociates into a very coarse sub-structure, which results in negligible strain-hardening, so that the creep rate becomes approximately constant soon after the load is applied. It seems unlikely, therefore, that the application of load under the same test conditions would cause the specimen pre-strained at room temperature, to dissociate into a still smaller sub-structure. It may thus be assumed that some other process is responsible for the observed decreasing creep rate; since the observations discussed earlier show that a growth of the sub-structure does occur during subsequent creep deformation, it may result from some type of softening process connected with the very early stages of growth of the sub-structure.

3. RELATION TO RECOVERY

Recovery is usually regarded as consisting of those changes that may occur during the heating of a deformed metal, before the onset of recrystallization. It is now known that recovery may involve certain observable alterations in the deformed structure.^{6,7} Without considering these in detail here, it may be stated that there is a considerable difference in magnitude between the effects of ordinary recovery and those due to the creep deformation, where the pre-strained specimen is subjected to combined heating and straining. To illustrate this, it may be seen that a specimen strained 5% at room temperature and heated for 1950 hr. at 250° C. (Fig. 15, Plate LXV) shows a large number of fine reflection spots, indicating that some "recovery" of the structure has occurred. However, it will be noted that the continuous diffraction line is not completely removed, so that the reflection spots appear diffuse. Comparison with an identical specimen subjected to combined straining and heating for almost the same length of time at 250° C., reveals that the growth of the sub-structure is far more pronounced in the latter case; the X-ray photograph (Fig. 6) consists only of well-defined reflection spots, without any evidence of the diffuse background associated with the initial slip structure. Moreover, the changes in structure of the creep specimen are far more pronounced even for much shorter times at temperature, as can be seen by comparing Fig. 5 with Fig. 15.

The contrast between the changes produced by heating alone and by creep deformation was also observed at 350° C., as illustrated by a comparison of Fig. 13 with Fig. 9. The changes due to recovery at 350° C. (Fig. 13) are more marked than at 250° C. (Fig. 15). With further heating at 350° C. the deformed specimen enters the recrystallization stage;

the X-ray photograph (Fig. 14) shows that partial recrystallization has occurred after 265 hours' heating.

Furthermore, the marked growth of the sub-structure during the second stage of the creep deformation is a consequence of the combined straining and heating rather than of heating alone. Accordingly, a specimen unloaded just after the creep rate begins to increase, and held at temperature for prolonged periods of time, shows no obvious change in structure.

It may be concluded, therefore, that the growth of the sub-structure produced by heating alone is negligible compared with that produced by combined straining and heating. Hence, the straining plays an essential part in initiating the growth.

4. RELATION TO RECRYSTALLIZATION

It has been mentioned above that with continued heating of the deformed specimen at 350° C., recrystallization occurs. On the other hand, an equivalent specimen subjected to combined straining and heating at 350° C. under a constant load of 250 lb./in.², as described earlier, showed no tendency to recrystallize, however prolonged the creep deformation. It appears that the continued growth of the sub-structure resists recrystallization. The same result could be obtained at 250° C.

Some further observations were made, however, which do not conform to this general behaviour. Recrystallization was observed during the creep extension of a pre-strained specimen, and furthermore it appeared to occur in a shorter time than for an equivalent specimen heated in the free condition at the same temperature. This result was obtained on a specimen pre-strained 5.2% at room temperature as before, and then extended under a constant load of 150 lb./in.² at 350° C. The observation was not confined to an isolated specimen, a similar result being obtained on a number of equivalent specimens strained under identical test conditions. It should be pointed out that the annealed specimen, strained under the same conditions of load and temperature, exhibits the stage of boundary micro-flow,³ where the metal extends without any detectable break down of the grains at all. Accordingly, the experiment was performed on the pre-strained specimen, to determine whether the original annealed state could be restored by combined straining and heating at 350° C.

The changes during the creep deformation of the pre-strained specimen, as revealed by X-rays, are illustrated in Figs. 16-18 (Plate LXV). The initial pre-strained state is similar to that in Fig. 3. The condition after 0.52% creep extension at 150 lb./in.² is shown in Fig. 16; the original continuous arcs have been replaced by discrete reflection spots, although there is still evidence of a diffuse background. These changes are similar to those observed on an equivalent specimen strained under the higher load of 250 lb./in.², for about the same amount of creep strain (Fig. 8). Fig. 17 illustrates the condition after 0.94% creep extension; a considerable change in structure has

occurred, and partial recrystallization was observed in a number of areas along the length of the specimen. The specimen continued to recrystallize on further extension, and after 1.5% creep extension had almost entirely recrystallized; Fig. 18 shows an area which has completely recrystallized, the X-ray photograph indicating a very coarse grain-size. Moreover, recrystallization was observed in the creep specimen after 141 hr., whereas the equivalent pre-strained specimen which was simply heated for the same period at 350° C., showed no evidence of recrystallization. Furthermore, after 265 hr. the creep specimen was almost fully recrystallized (Fig. 18), whereas the specimen heated for the same period in the free condition exhibited only partial recrystallization (Fig. 14).

The creep curve of the pre-strained specimen (curve *H*) is shown in Fig. 19. The corresponding

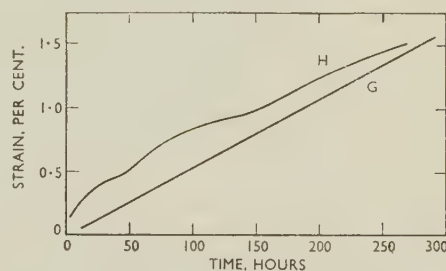


Fig. 19.—Creep of High-Purity Aluminium at 350° C. Under a Constant Load of 150 lb./in.².

Curve *G*. Annealed specimen.

„ *H*. Specimen pre-strained 5.2% at room temperature.

creep curve of an annealed specimen (curve *G*), extended under the same load and temperature, is included for comparison. The first feature is that the initial creep rate of the pre-strained specimen is more rapid than that of the annealed specimen. The second feature is that while the creep rate of the annealed specimen remains constant over the range of extension considered, the creep rate of the pre-strained specimen is continually changing. In this connection, it is known that when recrystallization occurs during creep deformation the creep rate increases.^{8,9} The fluctuations in creep rate shown in Fig. 19 are then most probably due to the fact that recrystallization occurs at various stages of the extension. It seems doubtful, however, whether the initial rapid creep rate can be attributed to recrystallization, since recrystallization was not observed at 0.5% creep extension. Also, this initial stage of decreasing creep rate occurred during the extension of an equivalent specimen strained under the higher load of 250 lb./in.², in which, as mentioned earlier, no recrystallization was detected. The third feature is that the average creep rate of the pre-strained specimen tends to become less than that of the annealed specimen. This behaviour may be expected, in view of the fact that the pre-strained specimen does recrystallize into a larger grain-size, and it is known that an increase of grain-size raises the creep strength of a metal.^{10,11}

IV.—DISCUSSION AND CONCLUSIONS

(1) The preliminary fine sub-structure, produced by the pre-straining, grows during the subsequent creep deformation. The sub-structure ultimately becomes of the same size as the equilibrium structure developed in a specimen strained from the initial annealed state, under the same load and temperature. The size of the equilibrium structure is governed, therefore, by the conditions of the deformation, regardless of the initial crystalline state of the metal. This result is in agreement with that obtained by Wood and Suiter,¹² where pre-strained specimens of aluminium were extended under constant rates of strain at elevated temperatures.

(2) The equilibrium structure formed in the specimens pre-strained at room temperature appears to be attained by a two-stage process.

The first stage of the creep deformation, corresponding to an approximately constant rate of creep, seems to be associated with the removal of the lattice distortion due to the initial slip structure. Although some growth of the sub-structure occurs at the same time, the creep rate remains constant until all traces of the slip structure have been removed.

The second stage of the creep deformation, corresponding to an increasing creep rate, is associated with a marked growth of the sub-structure. In this connection it should be pointed out that previous work on annealed aluminium has shown that, as the creep rate increases at any given temperature of deformation, the sub-structure tends to a smaller size. The growth of the sub-structure in the pre-strained metal must, therefore, be the cause and not the result of an increase of creep rate. Moreover, evidence is now available that metals flow particularly easily while internal changes, such as recrystallization,^{8,9} phase changes,¹³ and precipitation, including growth of precipitated particles,^{13,14} are occurring during the creep deformation. Accordingly, the growth of the sub-structure presumably takes place by some process involving considerable atomic mobility, and produces "position-change plasticity" (after Becker¹⁵), similar to the changes mentioned above, which results in an increase of creep rate. The observation that the creep rate of the pre-strained specimen eventually becomes comparable to that of the annealed metal, when both are extended under the same load and temperature, has also been made on lead alloys.¹⁶

In discussing a two-stage process, reference has been made to an initial decreasing rate of creep. It is considered that this does not represent a stage of transient creep, since a softening rather than a strain-hardening process appears to be involved. Further studies of the changes occurring in these very early stages of the creep deformation are required; it may be necessary to refer to a three-stage process.

(3) The combined straining and heating is far more effective in activating the growth of the sub-structure within the grains than is the heating alone. Previous observations confirm this.^{2, 4, 12, 17}

(4) In general, the changes in structure produced by the combined straining and heating resist recrystallization. For the experimental conditions considered, recrystallization normally involved heating the deformed specimen for at least a few hours. Recrystallization then occurred in a pre-strained specimen which was heated only, but not in an equivalent specimen subjected to creep deformation. This result might be expected, since, for comparable periods of time at temperature, the creep deformation is far more effective in removing the distorted regions of the metal, where nucleation can occur.

Under certain test conditions, however, namely low load (150 lb./in.²) at 350° C., recrystallization did occur during the creep deformation of the pre-strained specimen. The recrystallization appears to take place in a shorter time than in a corresponding specimen only heated at the same temperature. On the other hand, an equivalent specimen strained under a higher load (250 lb./in.²) at the same temperature, showed no evidence of recrystallization. Further studies are obviously required before any explanations for this behaviour can be advanced.

(5) Finally, considering the results in relation to certain more general issues, prior deformation has a beneficial effect on aluminium, provided, of course, that recrystallization is not a complicating factor; the steady-state creep rate is reduced and the life to fracture is correspondingly increased.

ACKNOWLEDGEMENTS

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REFERENCES

1. G. R. Wilms and W. A. Wood, *J. Inst. Metals*, 1948-49, **75**, 693.
2. W. A. Wood and R. F. Scrutton, *ibid.*, 1950, **77**, 423.
3. W. A. Wood, G. R. Wilms, and W. A. Rachinger, *ibid.*, 1951, **79**, 159.
4. G. B. Greenough and E. M. Smith, *ibid.*, 1950, **77**, 435.
5. D. McLean, *ibid.*, 1948, **74**, 95.
6. C. Crussard, *Rev. Mét.*, 1944, **41**, 111.
7. R. W. Cahn, *J. Inst. Metals*, 1949, **76**, 121; 1951, **79**, 129.
8. J. N. Greenwood and H. K. Worner, *ibid.*, 1939, **64**, 135.
9. W. F. Brandsma and E. M. H. Lips, *Z. Metallkunde*, 1936, **28**, 381.
10. C. L. Clark and A. E. White, *Proc. Amer. Soc. Test. Mat.*, 1932, **32**, (II), 492.
11. D. Hanson, *Trans. Amer. Inst. Min. Met. Eng.*, 1939, **133**, 15.
12. W. A. Wood and J. W. Suiter, *J. Inst. Metals*, 1951-52, **80**, 501.
13. K. Yamaguchi and K. Nakamura, *Rikwagaku Kenkyū-jo Ihō*, 1935, **14**, 76.
14. C. H. M. Jenkins, E. H. Bucknall, and E. A. Jenkinson, *J. Inst. Metals*, 1944, **70**, 57.
15. R. Becker, *Z. techn. Physik*, 1926, **7**, 547.
16. L. M. T. Hopkin and C. J. Thwaites, *J. Inst. Metals*, 1953-54, **82**, (4), 181.
17. J. Hino, P. G. Shewmon, and P. A. Beck, *Trans. Amer. Inst. Min. Met. Eng.*, 1952, **194**, 873.

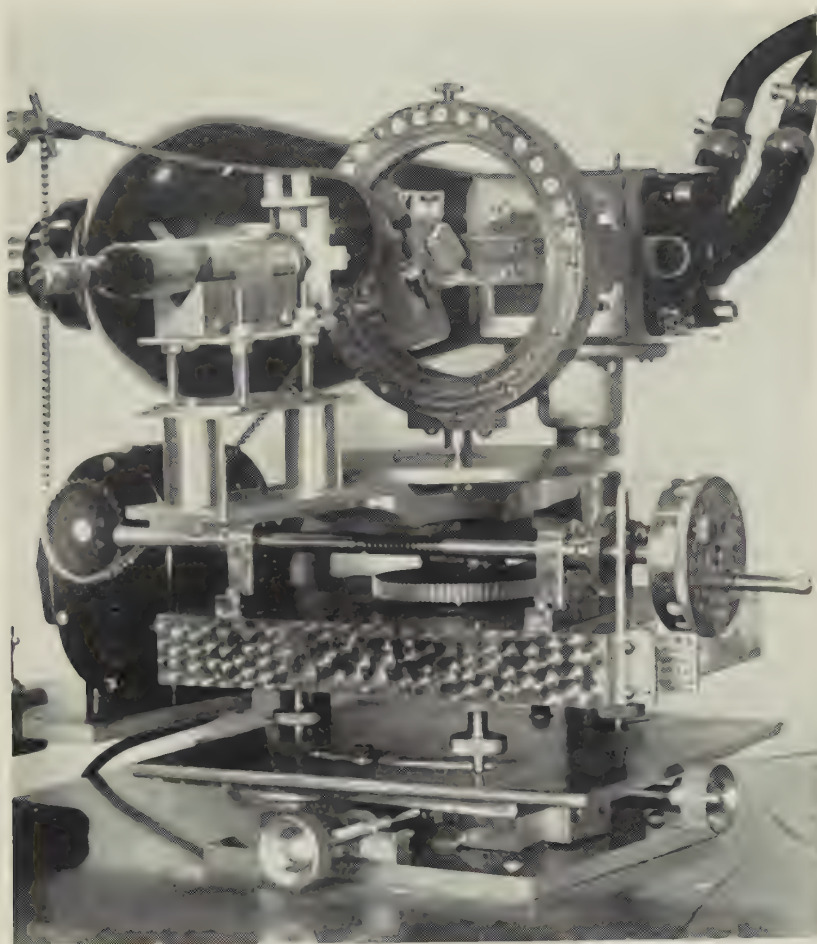


FIG. 3.—Experimental Arrangement for Schulz Technique.

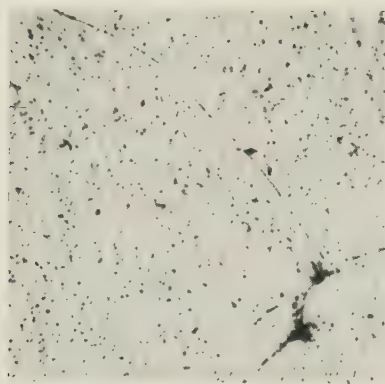


FIG. 4.—Polycrystalline Copper-0.05% Aluminium Alloy, Internally Oxidized at 900°C. Unetched. $\times 1000$.



FIG. 5.—Copper-0.3% Silicon Alloy Single Crystal, Internally Oxidized at 900°C. Etched in FeCl_3 Solution. $\times 750$.

Smith and Honeycombe

MICROSTRUCTURES OF SINTERED THORIUM.

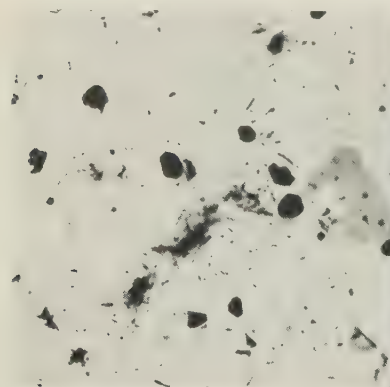


FIG. 5.—Sintered Thorium as Polished. The white phase frequently appears slightly darker than the matrix in unetched specimens. $\times 600$.

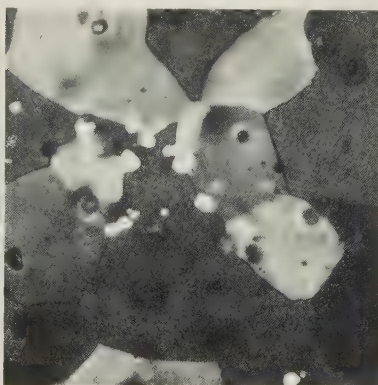


FIG. 6.—Inclusions of the White Phase in Resintered Thorium, Cold Worked and Annealed at 890°C. Electrolytically polished and etched. $\times 600$.

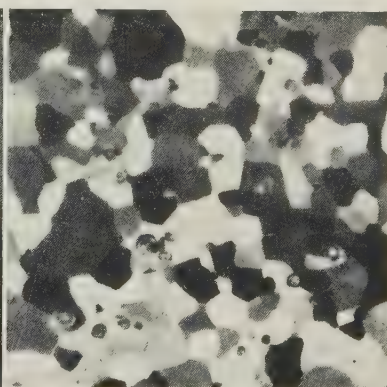


FIG. 7.—Resintered Thorium, Cold Rolled to 90% Reduction of Thickness and Annealed for 30 Min. at 700°C. Electrolytically polished and etched. $\times 400$.



FIGS. 3-6.—Pre-Strained 5% at Room Temperature and Extended Under a Constant Load of 700 lb./in.² at 250° C.

FIG. 3.—Initial strained condition.

FIG. 4.—Creep of 0.54% in 168 hr., showing changes during first stage of creep.
FIG. 5.—Creep of 1.8% in 735 hr., showing changes at beginning of second stage of creep.
FIG. 6.—Creep of 22% in 1850 hr., showing final equilibrium structure.



FIG. 7.—Annealed Condition.

FIGS. 8-10.—Pre-Strained 5.2% at Room Temperature and Extended Under a Constant Load of 250 lb./in.² at 350° C.

FIG. 8.—Creep of 0.57% in 23 hr., showing changes during first stage of creep.

FIG. 9.—Creep of 1.8% in 110 hr., showing changes at beginning of second stage of creep.

FIG. 10.—Creep of 25% in 352 hr., showing final equilibrium structure.

X-RAY PHOTOGRAPHS OF HIGH-PURITY ALUMINIUM.



FIGS. 11-12.—Pre-Strained 6.7% at 250° C. and Extended Under a Constant Load of 250 lb./in.² at 350° C.

FIG. 11.—Initial strained condition, showing no evidence of diffuse background.

FIG. 12.—Creep of 23.6% in 238 hr., showing characteristic equilibrium structure.



FIG. 15.—Strained 5% at Room Temperature and Heated in Free Condition for 1950 hr. at 250° C.; Showing

FIGS. 16-18.—Pre-Strained 5.2% at Room Temperature and Extended Under a Constant Load of 150 lb./in.² at 350° C.

FIG. 16.—Creep of 0.52% in 52 hr., showing a similar change to Fig. 8.

FIG. 17.—Creep of 0.94% in 141 hr., showing a similar change to Fig. 8.

FIG. 18.—Creep of 1.5% in 265 hr., showing a similar change to Fig. 8.

FIGS. 13-14.—Strained 5.2% at Room Temperature and Heated in Free Condition at 350° C.

FIG. 13.—120 hr. heating, showing changes due to recovery.

FIG. 14.—265 hr. heating, showing partial recrystallization.

By MAURICE COOK,† D.Sc., Ph.D., F.I.M.

SYNOPSIS

A survey is made of some of the most important developments that have taken place during the last thirty-five years in the wrought non-ferrous industry. Improvements in melting and casting procedures and the major innovations in rolling, tube manufacture, extrusion, thermal treatment, and other metal-processing techniques are briefly outlined, and some of the advances in copper, aluminium, and their alloys, and the advent of titanium as an industrial metal, are noted.

Reference is made to the importance and significance of impurities in, and small additions to, metals and alloys, to the joining of metals, particularly by welding, and some examples are given of outstanding advances in the technology of metal finishing.

Finally, mention is made of analytical control, especially by physical methods, and of inspection and testing techniques.

THANK you most sincerely for electing me your President for the coming year. This is an honour I deeply appreciate. Of the many duties that this office entails, one of the first is the delivering of a Presidential Address, and in thinking over the choice of subject and substance, as every one of my predecessors has had to do, I felt that, since I have been intimately concerned for so many years with the technical aspects of non-ferrous metallurgy, I might, in speaking to you today, refer to some of the discoveries, innovations, trends, and advances that seem to me to have been outstanding in their interest, or in their effect on the industry, and in enhancing the usefulness of its products.

I must first make it clear that I am not dealing with the industry as a whole, but more particularly, although not exclusively, with wrought non-ferrous metals and alloys. Again, I am not attempting to cover this field in its entirety, but confining my attention broadly to the period of my membership of this Institute, that is, from the end of the First World War to the present time. I am not seeking to review progress in general, or to essay the metallurgical history of these thirty-odd years. I am dealing essentially with technical matters, and not with the many notable contributions that have been made to progress in metallurgical science, or the several new and fascinatingly interesting fields of inquiry that have been opened up by recent researches. These disclaimers are registered because I know full well that I must perforce omit reference to many things which to you may seem, and perhaps quite rightly, much more important and significant than some of those I mention. As I have said, however, this is not an historical survey, but a noting of a few of those metallurgical happenings of recent years which have impressed me by their interest and importance.

This Institute was founded at a time when the industry for the most part was operating—on simple and, by present standards, relatively crude plant—

production methods based largely on empiricism, which for many decades had not appreciably altered. The material needs of the First World War and the general technical stimulus to which it gave rise, brought about a new dawn for the industry and initiated a forward movement the like of which it had never before experienced. Over the ensuing years this has continued apace. Now, manufacturing techniques are based on scientific principles and controlled by the application of scientific methods. The new knowledge that has become available, year by year in ever-increasing flow, from the research departments of industry itself, the universities and other educational institutions, research and development associations, and other research organizations, has made possible great improvements and the development of new processes and products.

In these years of rapid progress the activities of our Institute, and others of more recent origin with metallurgical affinities, have been of help and value to an extent which is possibly not fully realized or understood. It is not my intention here to elaborate this, but in its *Journal* the Institute provides, for the publication of papers and discussions, a medium of the highest reputation known the whole world over. Through its abstracting service it disseminates to its members a most comprehensive range of information, and the forum it has made available at its own meetings, those of its Local Sections, and also specially arranged meetings, has assisted metallurgical science and industry inestimably in promoting free discussion and in the exchange of views, opinions, and ideas on scientific and technical issues. The success of the Institute in these and other efforts to serve the varied interests of its members is, in some measure, reflected by the gratifying growth of membership in recent years, a continuation of which is essential to sustain its well-being and augment still further the scope, usefulness, and magnitude of its activities.

Despite the lingering survival of some antiquated

* Delivered at the Annual General Meeting, London, 30 March 1955.

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plants, the industry as a whole has undergone great changes in the space of a quarter of a century. The increased use of electricity for driving metal-working plant of all kinds, for metal melting, annealing and heat-treatment, and many other operations, has perhaps contributed more than any other single factor to this great transformation. The scale and speed of operations have been increased and quickened. Highly mechanized plants have largely replaced simpler and smaller hand-operated units. Where appropriate, continuous processes are being introduced in place of batch methods, and following the marked progress that has been made in instrument design, automatic control is being increasingly used. All these changes have raised production potential and efficiency, improved conditions of working, and eliminated much of the heavy manual labour that formerly and inevitably was associated with some processes. In addition to the advent of new manufacturing techniques and methods, the range of materials and products has been greatly extended to meet modern requirements. And now let me turn from the general, and consider, very briefly, a few specific matters.

MELTING AND CASTING

The associated processes of melting and casting are believed to date back to the Ubaid-Urak period of Mesopotamia, that is, about 3500 B.C. They are still the major initial or primary operations of that part of the metallurgical industry which concerns us here, and no metallurgist needs reminding that it is at this stage of manufacture that many of the imperfections and defects sometimes found in finished products have their origin. It is not surprising, therefore, that both processes have engaged the active attention of metallurgists for many years. Most of this work, which has occupied many investigators and ranged over all aspects of melting and casting, has fallen within the period with which I am dealing. At the beginning it was but a trickle, but with the passing of years it has greatly increased in volume, and I think it is in this field that metallurgists have made some of their greatest contributions to industrial progress.

Up to the time of the First World War, melting and casting practices were based almost entirely on the skill and experience of operatives, but with the advent of new alloys and the demand for increased output and castings of much greater size, the craftsman's skill alone was unequal to the task of improving or even maintaining ingot quality, and techniques based on scientific principles began to be introduced and have since been continued.

As long as forty years ago, the work of Sieverts and his collaborators indicated that molten metals dissolve large volumes of gases, the release of which during solidification might account for ingot unsoundness, and over the last thirty years metal/gas reactions have been the subject of much successful research. Conspicuous in studies of gas equilibrium with copper

has been the work of Allen and Hewitt on the combined effect of oxygen and hydrogen, and of Floe and Chipman on the role of sulphur. Gases in alloys, and their removal, have been studied for many years by the British Non-Ferrous Metals Research Association, and these researches have shown that in alloys not containing dissolved oxygen, and therefore not subject to the steam reaction, solution and subsequent emission of hydrogen is the major source of unsoundness, the remedies being suitable precautions in melting, removal of gas by presolidification, or treatment with a non-soluble gas such as nitrogen. In 1925 Portevin showed that additions of an oxidizing agent could eliminate unsoundness in gun-metal, and Lepp later proposed the use of oxidizing slags as a means of controlling dissolved gases in copper alloys generally. That hydrogen was a cause of unsoundness in aluminium alloy castings was recognized in 1929 by Claus, who showed that it originated from the decomposition of water by molten aluminium. This was confirmed in 1931 by Hanson and Slater, who, amongst others, demonstrated the efficacy of treatments with chlorine or nitrogen for the removal of hydrogen, procedures which have since become normal industrial practice.

Realization of the ill effects of gases led to the accelerated adoption of electric melting, utilizing arc, resistance, high- and low-frequency induction furnaces, and some of these have now almost entirely replaced other forms of melting in many sections of the industry.

The introduction of the copper-faced water-cooled mould, of the kind devised by Junker in about 1926, was a most noteworthy advance in casting practice, and water-cooled moulds of this type are quite generally employed in brass and copper mills. Their use in place of cast-iron strip and billet moulds has perhaps been responsible for a greater improvement in ingot surface, internal soundness, and crystal structure than any other modification in casting technique, and it has, moreover, greatly facilitated the production of large ingots of good and uniform quality, required for modern large-scale plants.

The use of continuous casting is another outstanding innovation, and the method originated by Junghans, some twenty-five years ago, has been successfully applied in the casting of brass alloys, and more recently for copper. The increase in demand for aluminium alloys in recent years focused attention on the need for better casting techniques. The production of sound ingots depends, amongst other things, on non-turbulent filling of the mould, and for many alloys rapid chilling is needed to obtain the necessary fine dispersal of phases. Following the lead of Junghans' work on the continuous casting of brass, in 1936 German investigations showed that by using a short mould and effecting most of the cooling by the direct application of water to the solidified ingot skin, a greater degree of chilling could be obtained than by conventional casting methods. Processes of this type, known as semi-continuous, proved to be so

successful in yielding good-quality products that they were rapidly developed. In less than ten years they became standard practice in the wrought aluminium industry throughout the world, and are now beginning to be used for the casting of copper and copper alloys.

Before I leave melting and casting I must mention the new technique that has been devised for metals of high melting point. Fifteen years ago it was used on a laboratory scale for melting very small amounts of metal, that is, buttons weighing only a few ounces, but now furnaces of this kind are in operation for producing ingots of up to 2 tons. Not only is it novel and interesting technically, but it is the only method at present known for melting in quantity such materials as molybdenum, titanium, zirconium, and their alloys. The metal is melted by means of an arc *in vacuo*, or in an inert atmosphere such as argon in a water-cooled copper crucible. The metal is either fed into the furnace as small pieces and an arc is struck between it and an electrode of tungsten or carbon, or the metal to be melted may itself constitute the electrode. In either case metal is melted by the heat of the arc and an ingot progressively built up, the molten pool being maintained at a constant depth either by raising the electrode or lowering the base of the copper crucible.

ROLLING

From slow, simple, ponderously driven machines, rolling mills have been transformed over a span of relatively few years into highly mechanized precision units capable of rolling heavy weights of metal accurately at high speeds. In general, it can be said that the rolling of long lengths of coil in wide widths reflects the chief difference in strip- and sheet-rolling practice today compared with that of thirty years ago, when narrow coils of small weight were produced by slow-speed rolling on two-high mills.

Broadly speaking, the beginning of the modernizing movement in non-ferrous strip rolling dates from about the second decade of this century, but it was not until the 1920s that it became appreciable. Since then two-high mills have been altered out of all recognition, and various types of multi-high mills have been devised and put into service. With these mills have come mechanisms for feeding, coiling, and tensioning, devices for the automatic adjustment of rolls and gauge, recording instruments, and other items of ancillary equipment to facilitate their efficient operation. Forty years ago the speed of cold-rolling strip mills rarely exceeded about 70 ft./min., but on modern mills speeds of about 1000 ft./min. are quite usual and speeds of 2000–4000 ft./min. not uncommon. The changes that have so altered rolling plant and practice have been born of the greatly increased demand in recent years for non-ferrous strip and sheet with the consequent need for speedier and more efficient production, the higher standards of quality required by users, and the need for suitable facilities for processing new and stronger alloys.

The early forms of two-high mills were greatly improved by the incorporation of such features as machine-cut gears, totally enclosed pinions revolving in oil, better bearings and lubrication, and mechanical adjustments for rolls, together with an overall greater accuracy in construction. These and many subsequent refinements have contributed to the evolution of the efficient two-high mill as we know it today. It is, however, the four-high mill that has marked the greatest change in rolling installations. Although the concept of such a mill is not new—indeed it was thought of by Leonardo da Vinci as far back as 1486—it was the need for suitable equipment for rolling strip many times wider than was the general practice thirty years ago that gave rise to the four-high mill. Mills of this type were first used in the U.S.A., where in 1926 a four-stand tandem mill was erected for cold rolling 36-in.-wide copper strip. A few years later four-high mills were erected in this country, and since then they have come into more general use, and for the hot and cold rolling of aluminium and its alloys in widths of up to 100 in., mass-production methods have been adopted to an increasing extent on lines similar to those used in modern continuous steel plants.

Other types of multi-high mills have more recently made their appearance, such as the Steckel mill in which all the energy of rolling is transmitted by the coiler and decoiler, and the Sendzimir mill with working rolls as small as $\frac{1}{4}$ in. dia., which not only reduces power requirements but facilitates rolling of strip in wide widths to thin gauges, particularly in harder alloys. For hot rolling, a recent and novel plant is the Planetary mill, which would appear to have considerable possibilities. On this mill, reduction is effected by a number of small-diameter rolls symmetrically disposed around the circumference of the rolls of a two-high mill, and it is possible to obtain, in one pass, a greater reduction than can be achieved in ten or more passes on conventional hot-rolling mills.

TUBE MANUFACTURE

Whilst some of the improvements effected in tube manufacture during the last twenty-five years relate to the production of tube shells, the most radical changes have been in drawing operations. Drawing on mandrels in short lengths, that is, about 20–30 ft., at speeds rarely exceeding 100 ft./min., on single-hole benches, was the method generally employed for many years, and the first major change began to take place in the early 1930s with the introduction of fixed-plug drawing, which made possible the processing of longer lengths at higher speeds and, moreover, the drawing of several tubes simultaneously. The years immediately following saw the further development of this method and also of the floating-plug technique, as well as multiple drawing, so that towards the end of the 1930s fully automatic triple drawbenches began to appear in the tube mills of this country, followed more recently by highly mechanized triple draw-

benches with capacities up to 300,000 lb. pull, capable of drawing tubes up to 150 ft. long, at speeds of about 350 ft./min.

The work on plug design, which made it possible to dispense with the plug rod and allow the plug to float, opened the way for block-drawing, in which tubing, reduced by conventional methods to 2 in. dia. or less, is further drawn on bull blocks, coiled after each draw and left either in long coils or alternatively straightened and cut to required lengths. This method has made possible the production of tubing in much greater lengths than could be formerly manufactured by other drawing techniques and at drawing speeds of up to 1800 ft./min.

Another departure from conventional bench drawing, particularly suitable for processing relatively hard alloys, is tube reducing, which was introduced about 1930.

The manufacture of steel tubes by welding is not only a long-established practice, but also a substantial proportion of the total output of steel tubing is produced in this way. It is, however, only very recently that techniques have been devised for the production of non-ferrous tubing by welding, and, although it is not part of my purpose in this address to speculate about the future, it would seem that for certain sizes of tubing, in some non-ferrous materials, methods of this kind may well prove to be both technically sound and economically attractive.

OTHER DEVELOPMENTS IN PROCESSING.

Markedly accelerated by the expanding use of light alloys, there has been in recent years a considerable growth in the output of extruded materials, and much has been achieved in improving the design and operation of extrusion presses and also in greatly increasing their capacity and range of products. Numerous interesting modifications have been made in extrusion practice, and amongst these some of the more important include the use of more durable materials for dies, mandrels, and other components, of glass as a lubricant, and the introduction of techniques for the production of hollow, tapered, and stepped extrusions.

As with extrusion, so in wire drawing many advances have been made in plant design, operation, and tool materials, resulting in greater efficiency. Of these the extensive use of tungsten carbide dies and the replacement of single-die units by high-speed multiple-die and tandem machines are two notable examples.

Furnaces for heating preparatory to initial hot working and for subsequent annealing and heat-treatment have all undergone many changes. The open-flame furnace long ago gave way to the muffle type, and the substitution of oil and gas for solid fuel facilitated improvements in quality and in temperature control. The more general use of electricity led to the development of a wide variety of types of furnaces too numerous even to mention, but associated

with some of them has been the added refinement, starting about twenty-five years ago, of annealing in such non-oxidizing atmospheres as burnt town's gas or burnt and cracked ammonia. Such furnaces have, moreover, made possible the high degree of precision in temperature control which has become increasingly necessary. Of other developments in thermal plant and practice, the use of induction furnaces for preheating and other heat-treatments is amongst the most recent and interesting.

I have referred only very briefly to the major operations involved in the manufacture of primary wrought products, but there are other techniques that have hitherto been used only to a limited extent, such as, for example, the direct processing of metal powders and electrodeposition. How far some of them could in certain circumstances be further usefully extended remains to be found out, but it would seem that they have perhaps not received as much attention as their possibilities would appear to merit.

COPPER AND COPPER ALLOYS

Before the period with which we are concerned, the copper alloys in general use were a range of brasses, gun-metals, tin bronzes, cupro-nickels, and nickel silvers. In all these groups, new and improved alloys have been produced in the past two or three decades, but many other new copper-base alloys have also been developed to meet the growing and varied needs of industry. To comment, however briefly, on all of these would occupy much more time than is available to me, and I propose therefore to pass by most of these special compositions of well-known groups and new alloys alike, that have resulted from careful, patient research and skilfully applied production techniques, and confine myself to two groups of alloys: one represents an important usage and illustrates much progress, that is, alloys for condenser tubes; the other, age-hardening alloys, have possibly an interesting future before them.

Before doing so, however, I feel I should refer to one or two outstanding features concerning copper itself. Unlike most basic metals, copper has been available in quantity in a highly pure form for many years, for electrolytic refining was started in this country as far back as 1869 and in the U.S.A. in 1883, and nowadays no less than 80% of the world production of primary copper is electrolytically refined. The contamination which arises from the melting of cathode copper in reverberatory furnaces caused attention to be directed to the possibilities of electric melting, and 1936 saw the installation of the first large-scale direct-arc furnaces for the continuous melting of copper cathodes, a practice which has since been widely adopted for the production of vertically and horizontally cast shapes of consistently high quality.

Until about thirty years ago, most of the copper fabricated in wrought forms was of the variety known as tough pitch, that is, it contained oxygen in amounts varying up to about 0.1%. During and towards the

end of the First World War, perhaps chiefly to facilitate the use of scrap by remelting without recourse to refining, and the production of tube shells by the piercing process, the expedient of adding a deoxidizer began to be increasingly practised in this country. It was not, however, until some years afterwards that investigations revealed the role of oxygen in copper, not only in melting, but in contributing to cracking and distortion of the metal when it was heated under reducing conditions, that is, in making copper susceptible to gassing. With this knowledge and the increased use, for example, of welding as a method of construction, the demand for copper immune from gassing began, some twenty-odd years ago, to gather momentum, until today most fabricated copper, other than that employed in applications where electrical conductivity is a paramount requirement, is, to the advantage of both producer and consumer alike, of the deoxidized kind.

In leaving this subject it is of interest to note that in about 1930 techniques were developed for the production, without the use of a deoxidizer, of oxygen-free copper, a material which while retaining the characteristically high conductivity of the metal, is also immune from gassing.

Ever since sea-going vessels have been fitted with condensers as part of their power-raising equipment, copper alloys have been used for condenser tubes. For many long decades 70 : 30 brass was the alloy generally employed both for this purpose and also in condensers for land power stations. As far back as 1890, Admiralty brass, essentially the same alloy with the addition of 1% tin, was in use as a superior product for more onerous service conditions. As these increased in severity, the problems, and the consequences, of condenser-tube corrosion became not only serious, but in some circumstances critical and grave.

In 1910 the Council of the Institute of Metals established a Corrosion Committee and inaugurated research on the subject of corrosion, especially of corrosion problems associated with condenser systems, and this work has continued up to the present day, that is, over a period of 45 years, a long time by any reckoning for a sustained research effort in one fairly narrow field. In that time the subject, which is most complex, has been studied from many angles. Much has been learned of the nature of corrosion processes, innumerable laboratory experiments and field trials have been carried out, the causes of many corrosion troubles that once were chronic have been tracked down, novel and valuable testing procedures have been devised and greatly improved, and far more serviceable materials have been developed and are now being produced. The first report to the Corrosion Committee of the Institute was published in 1911 in Vol. 5 of the *Journal* and the eighth and last in Vol. 40 in 1928. With these reports and the investigations they describe, the name of Bengough is particularly associated. In 1930 the responsibility for the work was transferred to the British Non-Ferrous Metals Research Association and under its ægis has continued

with unabated vigour and conspicuous success. At the same time industrial concerns pursued their own investigations and developments in the same field. It can, I think, be fairly claimed that the work done in this country has been mainly responsible for solving the major problems of condenser-tube corrosion, and for the development of corrosion-resistant alloys which have since become so widely used throughout the world.

Condenser tubes of 80 : 20 cupro-nickel were first made in 1921 in this country. In 1925 this alloy was superseded by 70 : 30 cupro-nickel, which was shown to be markedly superior, and tubes of this latter alloy, after approval by the Admiralty, were adopted in 1927 as standard for the Royal Navy and formed the subject of a specification in 1930. Investigations which stemmed from the variability of performance of tubes in service showed that relatively small amounts of iron and manganese, especially the former, greatly improved the resistance of the alloy to corrosion, and particularly to impingement attack. In consequence the specification was modified in 1934 to include iron plus manganese and later changes cover up to 1.0% iron and 1.3% manganese. This is the type of cupro-nickel that has been developed after years of experiment and experience, and is now generally fitted in the condensers of naval vessels and large ocean-going liners, and used in many land power stations where the condensing systems have to contend with severe corrosive conditions.

At one time it was thought that aluminium in brass impaired the corrosion-resistance of the alloy, but work done in the early 1920s at Woolwich for the British Non-Ferrous Metals Research Association and later in the Association's own laboratories showed, on the contrary, that it was indeed most beneficial, and thereafter a brass of the α type containing about 2% aluminium was developed as a condenser-tube material. It would seem to have been first so employed in about 1929, and since then its use in this and other applications has continued to increase. The presence of this amount of aluminium also greatly improves the resistance of brass to oxidation at elevated temperatures, for at 775°C., for example, the rate of oxidation is only about one-fortieth that of a straight brass.

Later, I shall be making a few observations about the effect of impurities and small alloying additions, but I can appropriately mention one example now. Corrosion which gives rise to dezincification in brass alloys was at one time a serious trouble, and the investigators to the Corrosion Committee of the Institute, to which I have referred, devoted much effort to studying the causes and prevention of dezincification. In about 1923 a considerable variability of performance in service of brass condenser tubes was traced to the presence or absence of arsenic. This observation was confirmed, and for the past thirty years it has been a common, if not general, practice in this country to add arsenic in amounts of about 0.02–0.05% to α -brass alloys for service where resistance to corrosion is an important consideration.

As a footnote to this work on condenser-tube materials, I might add that the British Non-Ferrous Metals Research Association extended its studies to the effect of iron on alloys of lower nickel content, and alloys of this range of composition, that is, up to about 10% nickel with iron contents up to 2%, with good corrosion-resistance and capable of easy manipulation, have been developed for other sea-water-carrying pipes in ships and power stations.

The use of copper alloys extends over thousands of years, and their production has featured in the industrial development of this country for centuries. Despite this long history, nothing was heard of heat-treatable copper alloys until about the middle of the 1920s. At that time the investigations of Corson, Masing, Fraenkel, and others revealed that several copper alloys could be hardened by heat-treatment alone. The outstanding example was the copper-beryllium alloys, which, with other alloying additions, were studied in considerable detail and have since been developed more than any other heat-treatable copper alloys. Since then the number of age-hardenable copper-base alloys which have been found runs into hundreds. Many of these have not been studied in any detail, but a few, notably those containing nickel with additions of silicon, aluminium, manganese, tin, or phosphorus, and those containing chromium, have been used industrially to some extent, and papers dealing with some of them have appeared in the *Journal* of this Institute. As Merica said more than twenty years ago in speaking of alloys which are hardenable by heat-treatment alone, such alloys may be the rule rather than the exception amongst alloying systems.

Although there are many uses for some of these alloys, the total amount of them produced is trifling in relation to other copper alloys, and thus their relative importance is very different from that of the heat-treatable alloys in the aluminium industry. There, the discovery of age-hardenable alloys opened up a wide vista of possibilities for aluminium, when that metal was still in its infancy, and the development of alloys of this type contributed greatly to the growth of the light metals industry and are today an important part of its production. For the purposes for which many of the more familiar copper alloys are, and have been, generally used, their physical and mechanical properties are suitable and adequate, and the discovery of heat-treatable alloys went unheralded and made no perceptible industrial impact. However, whilst such special uses as there are for those heat-treatable copper alloys available in wrought forms, do not at present involve the consumption of more than modest tonnages, the ever-increasing volume and variety of new developments in many fields suggest that this situation is one which could rapidly and appreciably change. Knowledge of most of these alloys extends little beyond an approximate determination of their constitution, and only for a few alloys is any detailed information about physical properties available. Many of the alloys are difficult

to produce, and some require prolonged thermal treatments for optimum properties to be obtained. The known alloys of this type, as well as those not so well known, would seem to merit further investigation, of both a fundamental and technological kind, since some of them have interesting properties about which more could, with advantage, be learned. Moreover, for the further development of these materials more information is needed about the nature of the hardening processes that take place, including the possibility of drastically shortening the prolonged thermal treatments sometimes required to obtain optimum properties.

ALUMINIUM AND ALUMINIUM ALLOYS

From an annual level of some 5000—10,000 tons at the beginning of the century, the world production of aluminium has risen to about 3 million tons in 1954, and in this country the output of semi-fabricated products in this metal and its alloys has increased three- or four-fold in the last fifteen years. This spectacular growth in the production of these materials reflects the greatest change that has taken place in the pattern of production of wrought non-ferrous metals in modern times. Associated with this vast expansion, there have been improvements in production technology of a most impressive kind, and also in further fabrication and finishing processes, to one or two of which I shall refer briefly later.

The purity of aluminium made by the reduction of alumina normally ranges from about 99 to 99.8%, and whilst most of the current output consists of qualities in that range of composition, high-purity aluminium is becoming more and more important. This grade, with a purity of upwards of 99.99%, is produced by a second electrolytic process involving the three-layer refining cell, and its manufacture on an industrial scale, which started about the mid-thirties, is one of the most important new features in aluminium production since Hall and Héroult introduced their reduction process in 1886. Valuable attributes such as increased corrosion-resistance, workability, and thermal and electrical conductivity, as well as excellent anodizing properties and high reflectivity, understandably account for the increasing use of this quality of aluminium and, moreover, its use in making certain alloys is growing and would seem likely to continue.

Most of the types of aluminium alloy now in use have been known for a long time, but over the years many modified versions with better properties have been developed from their predecessors. Although there seems to be a large number of compositions in use, the principal alloys all fall essentially into six groups: the three non-heat-treatable series, aluminium-manganese, aluminium-magnesium, and aluminium-silicon, and three heat-treatable types based on the aluminium-copper-magnesium-silicon, aluminium-zinc-magnesium, and aluminium-silicon-magnesium systems. The strongest of the heat-

treatable alloys so far produced, that is, those containing zinc and magnesium, made their appearance about twenty years ago, and these, with the modified aluminium-silicon alloys, are amongst the most important and interesting developed in the period. The magnesium-silicide alloys and those containing magnesium are older groups, but in recent years they have been much improved and largely used in transport, structural, and marine applications.

Although the cladding of one metal with another is quite an old practice, it seems to have first come into the aluminium field only about thirty years ago in Germany, when techniques were devised for coating, with aluminium, heat-treatable alloys of the Wilm type—that is, with copper, magnesium, and silicon as the essential alloying elements—as a protection against corrosion. Since then this practice has been adopted quite generally in this and other countries, and it has been extended to coating materials other than aluminium, such as an aluminium-1% zinc alloy, which, being anodic to the core material, provides some measure of sacrificial protection. Clad aluminium alloys have become important products, and this form of protection is probably used in much greater proportion with aluminium than with any other metal.

EFFECT OF IMPURITIES AND SMALL ADDITIONS

From the results of research of immediate technological interest that has been going on in recent years, we know enough about impurities and their influence on metals to appreciate not only the beneficial effect of high purity, but also that a pure material is not always, and in all circumstances, better than one which is less pure. From this work we have learned much in a few years and we know, for example, that small amounts of elements fortuitously present, or deliberately added to a metal, can affect its properties, or some of them, to a pronounced degree. We know also that the purity not only of the parent metal but also of the alloying metals can markedly influence the quality, properties and serviceability of the resulting alloy. This whole question of the purity of metals and alloys is one of the greatest importance and significance in both their processing and use, and the successes achieved in producing primary metals to high-purity standards must certainly rank amongst the most outstanding advances made in the past two or three decades.

Usually the corrosion-resistance of a metal increases with its purity. With magnesium, which affords a notable example of this, remarkable improvements have been obtained in the corrosion-resistance of the metal itself, its alloys, and alloys in which it is a major constituent, by reducing the amount of impurities. Aluminium is another well-known case where availability of high-purity metal has had a significant effect on the extended uses of the metal itself and also on its alloy technology. But the light metals are not

alone in this, and other base metals too can now be obtained in high-purity grades. The advent, in the middle twenties, of high-purity zinc, that is, not less than 99.99%, provided a turning point in the evolution of zinc-base die-casting alloys, which represent the most notable single new use for zinc developed during this century. Castings in these alloys that had so far been produced were prone to distortion, corrosion, and dimensional instability, and the work in 1922 of Brauer and Peirce, which showed that this was associated with the presence of small amounts of tin, lead, and cadmium, pointed the way to the production of vastly superior castings by using alloys made from high-purity zinc.

Just how significant the restriction, to a low limit, of a commonly occurring impurity can be in influencing production practice is illustrated by lead in α -brass. Until a few years ago, it was usual in making strip and sheet in α -brass alloys to cold roll throughout. With the need for processing much larger ingots into wider and longer coils, the attractiveness of initial hot rolling was clear enough, but only became possible and generally adopted, as it has been, by limiting the lead content to a maximum of 0.02%, although other considerations and some specifications would tolerate a much higher figure.

I have already mentioned the important use that is made of small quantities of arsenic in inhibiting dezincification in α -brass, and more recently it has been found that antimony and phosphorus have a similar effect. It is, however, not known how this inhibiting effect is brought about or why it happens in α -brass but not in other brasses.

There are also many instances of the remarkable and beneficial effects which can be produced in well-known alloys, both ferrous and non-ferrous, by small additions of elements other than the alloying ingredients themselves. I will mention but two. Aluminium-silicon alloys nowadays are a familiar group of light foundry alloys, and although they have been known for a very long time, they attained industrial importance only after Pacz had shown, in 1920, that the properties of the eutectic alloy could be vastly improved by the addition of small amounts of sodium or other alkali metals. Much more recently we have had a comparable example of beneficial structural modification in the production of nodular cast iron by inoculation of the melt with a small quantity, that is, about 0.1 or 0.2%, of cerium or magnesium, and irons so treated are far stronger and tougher than those in which the graphite is present in the usual flake form.

There has been no tardiness on the part of industry in making use of these and many other such discoveries and findings, some of them accidental and most of them empirical, concerning the effect of small amounts of added elements. The results have frequently been so very rewarding that it is surprising much more work has not been done to obtain a fuller understanding of these effects and how they are brought about, and I cannot but think that studies in

this field merit more prominence and a greater share of the available research effort than they receive at present.

TITANIUM AS AN INDUSTRIAL METAL

The last few years have seen the advent of titanium as a new industrial metal, and the technical achievements that have made this possible are amongst the most interesting in the period with which I am concerned. The whole production of titanium and its alloys is dominated by the need for, and the difficulty of, avoiding contamination by impurities, and the history of this metal and its technology provides surely one of the most vivid illustrations of just how important impurities can be.

Titanium was discovered in 1790, but for 135 years knowledge of its properties was hidden from us by the masking effect, as we now know, of impurities such as oxygen and nitrogen in particular. Before 1925, it was known only as a brittle, unpromising metal, but in that year the Dutch chemists van Arkel and de Boer produced metal of about 99.9% purity, which was quite different from that hitherto made, inasmuch as it was very ductile and readily workable in the hot and cold states. Elegant though it was, the method used by van Arkel and de Boer of thermally dissociating the tetraiodide of titanium formed at much lower temperatures, could not be, and has not yet been, translated into an industrially workable process. However, as a result of their work it became possible to determine the real properties of titanium, and this information pointed the way to an important and growing future for the new metal. The worthwhile objective was there for the development of a less costly extraction process which would yield acceptably pure metal. To Kroll, working at that time in Luxembourg, goes the credit for devising and developing the first process to be used on an industrial scale for the extraction of titanium. In 1940 he was granted a patent for the production of titanium by reduction of the tetrachloride with metallic magnesium, with subsequent removal of the residual magnesium and magnesium chloride by leaching. This pioneer work was continued in the U.S.A. under the auspices of the Bureau of Mines, and details of the various techniques developed were made known in 1946. Industrial production started modestly in the U.S.A. in 1948 with an output of about 15 tons. In 1954 this figure probably reached, in total for the world, although most of it was American, about 4000 tons, and the capacity of existing and projected plant in the U.S.A. is reputed to be about 35,000 tons a year. It has been suggested that the demand could soon reach six figures, and it would seem quite probable that an output of this magnitude might well be achieved in the next few years.

JOINING METHODS

Metallurgical methods of joining metals together, that is, welding, brazing, and soldering, have, of

course, been practised for centuries, but new materials and new uses have greatly increased the importance of this branch of metal technology. The rapidly growing use of welding in metal fabrication and utilization is now too well known to need any emphasis, and it will be recalled that in 1923 the Institute of Welding was established. In 1936 this body formed a Research Committee which, in 1938, became the Welding Research Council and, in 1946, the British Welding Research Association, an organization which since its inception has been responsible for many investigations that have contributed much to the advancement of welding in both the ferrous and non-ferrous fields.

Particularly over the last twenty years, a vast amount of work has been carried out on the metallurgy of welding processes, and this has led to many notable developments in welding practice and the increasing use of welding as a method of construction. It is in this period, and as a result of this work, that so much progress has been made in the welding of non-ferrous materials, which before then was but an indifferently successful and not very extensively used joining technique. For fusion welding, the processes so usually and satisfactorily employed for steel—that is, gas, metal-arc, and carbon-arc welding—were adopted in the absence of others, for welding non-ferrous metals, but they have not generally proved suitable for the production of high-quality welds.

It was the advent during the war years of the argon-arc process, and subsequently of the argon-shielded metal-arc process, that so greatly changed the position in providing a means whereby consistently sound strong joints could be produced in such materials as aluminium- and copper-base alloys. In these processes the use of flux, with its attendant disadvantages, is not necessary, since the heated metal is shielded from the atmosphere by a blanket of inert gas. Moreover, the high rates of heat input that can be achieved are of particular value in welding materials of high thermal conductivity, and enable heating to be confined and so minimize cracking and distortion. In the argon-arc process, either direct or alternating current can be used, and with the latter, in the half cycle in which the electrode is at positive potential, a cleaning action, essential in welding such materials as aluminium, magnesium, and aluminium bronze which possess resistant oxide films, is effected on the metal surface. In the argon-shielded metal-arc process a similar result is obtained, and because of the very high current density in the electrode wire, and consequently the strong magnetic field surrounding the arc, the metal is transferred as a narrow column of fine spray rather than as droplets. This directional effect, which is so pronounced that welding can be carried out in all positions, and the high thermal efficiency which results in high rates of metal deposition and consequently high welding speeds, make the process especially attractive for constructional work.

Although argon-arc welding has been the most outstanding new feature in non-ferrous welding prac-

tice in recent years, the considerable progress made in resistance spot and seam welding has led to a greatly increased use of these techniques for joining aluminium alloys. In joining them by methods other than welding, the use of organic bonding agents resulting from the work of de Bruyne, and of brazing techniques devised from the investigations of Miller and others, are amongst the most important new methods developed.

METAL FINISHING

Although it is the properties of metals which largely dictate their use for any particular purpose, it is a common practice, either for decorative or protective reasons, to coat them with other metals or with non-metals such as paints, enamels, plastics, and lacquers. This whole subject of finishing treatments for metals, either as intermediate products or finished components, is one to which much attention has been given in recent years. A technical organization devoted exclusively to it, the Institute of Metal Finishing, was founded in 1926 as the Electrodepositors' Technical Society, and has been very active and successful in disseminating knowledge and stimulating interest in the subject. The field is a very wide one, and there are many examples of outstanding interest that could be cited, but I will mention only three, namely chromium plating, anodic oxidation, and sprayed metal coatings.

Although the technical achievements associated with the development of chromium-plating techniques and practices would perhaps not be rated as exceptionally high, this particular form of metal finishing by electrodeposition is one of the most widely used. From being a somewhat unreliable but attractive novelty thirty years ago, it is now to be seen any day and every day indoors and outdoors. Its importance not only derives from its use as a decorative or protective finish, but also from its application as a hard-surfacing material for drawing dies, for example, and in building up worn parts.

It was as far back as 1856 that Geuther first electrodeposited chromium from a chromic acid solution, and although Carveth and Curry indicated the commercial feasibility of such a process, it was not until the 1920s that it was taken up industrially. The pioneering work of Sargent formed the principal foundation for this activity, and the increased use and industrial success of chromium plating is due not so much to improvements in the composition of the bath, as to a proper understanding of the operational control that is necessary.

Anodizing or anodic oxidation must nowadays be as familiar to the general public as chromium plating, and the development of these two forms of metal finishing has been almost coincident in time. Anodizing was unknown before 1923. In that year patents were granted to Bengough and Stuart covering the production of oxide films on aluminium anodes in chromic acid solutions, and also the colouring of such

films by immersion in aqueous solutions of suitable organic dyestuffs. Soon afterwards, the oxalic and sulphuric acid processes were developed, and in the years that have followed, the hundreds of patents that have been taken out concerned with techniques and applications of anodizing provide some indication of the interest engendered by this method of protecting aluminium and aluminium alloys against corrosion. Important though that particular use is, anodizing with subsequent coloration has developed extensively in recent years and become a most popular form of decorative finish. There is yet a third use of a more specialized kind, that is, hard surfacing. As a result of recent work, it is now possible to produce consistently, under conditions of industrial operation, thick and hard oxide films, which are being increasingly used under service conditions where a high degree of resistance to wear and abrasion is required.

Although they are quite different both constitutionally and in the methods of their production, inasmuch as one is a cathodically deposited metal and the other an anodically formed oxide, these two coatings, electrodeposited chromium and anodic oxide films, have in common, as we see, three major uses, namely, protection against corrosion, decorative finishing, and hard surfacing.

Another form of protection against corrosion, principally for ferrous materials, is metal spraying, and although it had its genesis outside our period—for it is based on the work of Schoop, whose essential findings are included in patents granted to him between the years 1910 and 1912—its successful development, especially in this country, began only ten years or more later. It is interesting to note in passing, that the first important paper dealing with this technique was published by Morcom, in the twelfth volume of the *Journal* of this Institute, as early as 1914. A great deal of effort has been applied to the development of equipment and techniques, and much study has been devoted to the nature of sprayed deposits and their resistance to corrosion. For protective purposes zinc was one of the first metals to be used and it is still the most important, but within the last fifteen years or so the protective value of sprayed aluminium coatings has in turn been investigated, appreciated, and developed. Its extensive use provides an indication of the important position metal spraying has now reached as an effective means of combating the ravages of corrosion in structural steel work and other equipment, and the technique has also been successfully applied to the building up of worn steel parts.

Tinplate, of course, is essentially a ferrous product, and in connection with metal finishing, or the coating of metals, I said I would content myself with references to three examples only, which I have indeed just done, but I feel constrained to mention tinplate also. This commodity accounts for about half the total consumption of tin, and its annual output, which runs into millions of tons, is produced in some of the most imposing plant employed in the metallurgical industry. The changes that have revolu-

tionized production methods have been the introduction of large powerful mills for rolling wide strip in coils weighing several tons, and of electrolytic tinning with the consequent creation of an effectively integrated large-tonnage, continuous process yielding a product of consistent quality. These plants indeed impress by their immensity, capacity, and efficiency, and the accomplishment of implementing, within one decade, research work on electro-tinning into a continuous industrial process on a vast scale, must surely rank as one of the most striking metallurgical successes of our time.

ANALYTICAL CONTROL

Since the properties of metals and alloys are so closely and largely determined by their composition, analytical control has always been a necessary and important feature in the wrought non-ferrous industry. Today it is, with the increased volume and variety of production, and the existence of an ever-increasing number of specifications with stringent compositional clauses, more important than ever. But apart from specification requirements, effective analytical control, which implies quickly available, accurate analytical results, is indispensable to many of the more recently developed processing techniques. Fortunately, considerable attention began to be directed years ago to the development of rapid and accurate analytical procedures, and the success that has attended these efforts, which very rightly and wisely have been continued, represents, in my view, an outstandingly valuable contribution to the progress of the industry. It seems to me doubtful whether the importance of this work, on one of the industry's ancillary but most essential services, has been generally or sufficiently appreciated.

Thirty years or so ago, analytical methods were generally based on classical chemical separations, the final determination being made gravimetrically or volumetrically. Although in the ensuing years there have been notable developments in chemical analysis, as for example, in micro-chemistry and chromatography, spectacular advances have been made in the use of physical instruments and methods for analytical control, and spectrographs are normal items of laboratory equipment.

In earlier years, estimation of a metallic constituent by means of the intensity of colour produced in a solution was effected visually with the aid of a device such as a tintometer. Absorptimeters became possible with the introduction of photo-electric cells of the barrier-layer type, which allowed ready quantitative measurement of the amount of light absorbed by the solution. Accuracy was subsequently further improved by employing mercury-vapour discharges, monochromators, and spectrophotometers, as well as by general advances in electronic design. The useful range of colorimetric methods was considerably extended thereby, while still retaining the advantages of speed and simplicity.

The spectrograph, however, has been by far the most useful of the various physical methods devised, for its successful application in non-ferrous analysis has made it possible for results to be obtained in the space of minutes rather than hours, or longer, with an enormous saving of man-power. The values of these techniques is reflected by the statement of Twyman to the effect that during the Second World War there must have been about 500 spectrographic outfits in use in Great Britain alone, for controlling the production of industry.

In this field, research was undertaken by the British Non-Ferrous Metals Research Association in 1925 and has continued ever since. It is a notable example of highly successful co-operative research. The first paper dealing with industrial applications of spectrographic techniques, published in 1923, recorded results obtained in an American laboratory with a British instrument, and the first papers on this subject in the *Journal* of the Institute appeared in 1931.

In the early years of their employment in industry, spectrographic methods were limited to the detection and estimation of small quantities, by means of visual examination of spectra recorded on photographic plates. Later, however, the barrier-layer photo-cell made possible the production of a micro-densitometer, with which densities of recorded lines could be accurately measured, thereby greatly extending the scope of spectrographic methods. The great advances in electronic design and components during the war led to a radical change in spectrographic procedure, by the use of electronic multipliers for recording, directly and immediately, the intensities of radiations. Direct-reading spectrometers became available in the U.S.A. in 1945, and they have been followed by others made in this country and elsewhere. As a class, they are certainly the most efficient analytical instruments so far developed, inasmuch as they provide for the accurate, rapid, and economical estimation of most, if not all, metallic elements.

The results of continuing work on other methods and current researches in X-ray fluorescence, mass spectrometry, and radioactivity indicate that the range of physical methods for analytical control may well be usefully extended in the future.

INSPECTION AND TESTING

Modern production techniques, and the exacting nature of the conditions which some metals are required to withstand in many uses today, call for much more than visual inspection of materials in process, and simple mechanical tests such as hardness, tensile, bend, and ductility tests, which almost entirely sufficed years ago for most products of the industry. Thus, in addition to notable advances in new products, plant, and manufacturing procedures, as well as in physical methods of controlling composition, the period has witnessed the introduction of many new inspection and testing techniques, of which I can but briefly mention a few.

Foremost among these is radiography, which has proved most valuable and is being increasingly applied in the examination of castings, forgings, and welds. In fact, the acceptance of welding as a method of construction for assemblies subject to severe service conditions, such as pressure vessels, was at least in part dependent on the availability of this method of inspection, and its importance in the examination of materials and components for aircraft needs no emphasis. The applicability of the technique to greater thicknesses of metal than can be penetrated by X-rays has recently been made possible by recourse to radioactive-isotope sources, the most powerful so far available being cobalt 60. For detecting deep-seated defects, ultrasonic methods, although not always so informative, have proved a useful alternative for examining large masses of metal which require long exposure times by radiographic techniques.

In the simplest forms of electrical-conductivity methods of examination, the changes in resistivity associated with dimensional and compositional differences are directly measured, but more elegant methods have recently been introduced in which resistance changes serve to influence the magnitude of eddy currents, and techniques of this kind are being used for assessing the internal conditions of tubing, flaw detection, and the inspection and thickness measurement of strip and sheet.

The large increase in the past quarter-century of processes and operations in which metals are used at elevated temperatures has necessitated the development of special mechanical-testing techniques. Although Andrade carried out important investigations into the phenomenon of creep in metals under stress at elevated temperatures as early as 1911, it was not until about 1923 that the work of Dickenson and others revealed the complete inadequacy of the ordinary short-time tensile test as a means of providing data for the design of plant to operate for long periods at high temperatures.

For certain types of plant or construction it is necessary to know, in addition to the stress which the metal will withstand for a defined long period, the extent to which creep or plastic deformation will occur in specified times at different levels of stress, to ensure, not only freedom from fracture during the expected working life, but also the limitation of deformation to tolerable amounts. Information of this kind is being required to an increasing degree, and consequently the determination of creep data has become an important activity of modern testing. Special machines have had to be designed and built, incorporating furnaces in which the specimens under test can be maintained for many thousands of hours under very closely controlled temperature, and fitted with devices enabling the amount of extension or creep to be measured with a sensitivity of a few

millionths of an inch at intervals throughout the test.

In addition to the production of results of immediate and practical value, which currently absorbs most of the capacity of creep laboratories in this country and elsewhere, interesting studies have been made of the nature and mechanism of creep, and whilst some investigations have been made of the effects on creep characteristics of such variables as small composition differences, grain-size, processing techniques, &c., much remains to be done in this field.

The period covered by this survey has seen the full realization of the need for information on the resistance of metals to alternating and repeated stresses. In the last century observant engineers had appreciated that the data of the simple tensile test were insufficient when related to structures and mechanisms in which the component parts were subjected to alternating stresses. Fairbairn, as far back as 1864, had studied the failure of riveted wrought-iron girders subjected to repeated stresses, and the classical work of Wöhler was published in 1871. It was, however, the increasingly onerous conditions which metals were called upon to withstand in aircraft and other equipment during the First World War that gave rise to the intensive study of fatigue, which began in the early twenties and still continues. A wealth of information has been produced during the past thirty or so years by workers too numerous to mention, with Gough in this country and H. F. Moore in the U.S.A. as outstanding contributors. Today, the determination of fatigue strength under different conditions forms an important activity of practically all research laboratories concerned with metallurgical matters. A large variety of testing equipment has been made available, including the simple rotating-beam type, the direct tension-compression type in which the tensile and compressive forces alternate about a mean other than zero, and machines for testing fatigue effects at elevated temperature. Although a great volume of useful and valuable fatigue and corrosion-fatigue data has been produced, covering a wide range of materials and corroding agents, our knowledge of the essential physical and metallurgical factors which cause failure by fatigue is still very limited.

During the thirty-six years since the end of the First World War, our knowledge of metals has been vastly increased and profoundly deepened. As a result of this, and the immense strides forward in production technology, in improving processes and products, and in developing new ones, the industry has grown greatly both in size and importance. Impressive as all these achievements have undoubtedly been, I think we can, with every confidence, look forward to still more outstanding advances in the future, and this Institute, I am sure, can and will help importantly in their fulfilment.

1618 THE EFFECT OF NITRIDES AND TERNARY INTERMETALLIC COMPOUNDS ON THE YOUNG'S MODULUS OF SOME ALUMINIUM ALLOYS*

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SYNOPSIS

Various binary and ternary aluminium alloys were prepared by chill-casting or sintering and extrusion, and their elastic properties were investigated. It was found that the presence of nitrides of aluminium, chromium, magnesium, iron, vanadium, and titanium caused an appreciable increase in Young's modulus. Ternary intermetallic compounds showed a similar effect, e.g. a substantial gain was observed in aluminium-iron-nickel alloys. The detrimental effect of magnesium was offset by additions of chromium or manganese, resulting in an improvement in Young's modulus. The relationship of the modulus to the composition and heat of formation of various intermetallic compounds is discussed.

I.—INTRODUCTION

As a result of an investigation^{1,2} into the mechanical properties of some aluminium alloys, it was found that their elastic modulus was improved by the addition of certain elements, and that this effect was proportional to the concentration of the added element. It was therefore thought that the presence of intermetallic compounds was responsible for raising the Young's modulus of certain of the alloys, and a suggestion was put forward that the most effective would be those compounds which have a high heat of formation. It was also pointed out that the improvement in Young's modulus for a given concentration of element would be greater, the larger the number of aluminium atoms in the compound.

The work now described had the following objectives:

(1) To study the effect of well-established ternary compounds in aluminium alloys with such metals as cobalt and beryllium, copper and beryllium, chromium and magnesium, iron and nickel, manganese and magnesium.

(2) To prepare, by melting or by powder-metallurgy methods, aluminium alloys containing nitrides of chromium, magnesium, iron, vanadium, aluminium or titanium. The heats of formation of the last two compounds were known to be exceptionally high.

II.—EXPERIMENTAL PROCEDURE

1. CHILL-CAST BARS

As in previous experiments,^{1,2} melts of about 3 lb. each of alloys having the following nominal compositions were prepared in a Salamander crucible heated in an electric furnace and cast into bars, 1 in. in dia. × 9 in. long, in a horizontal mould:

Ternary Alloys

- (a) (i) Be 1 + Co 2, 4, and 6%.
- (a) (ii) Co 1 + Be 2 and 4%.
- (b) Be 1 + Cu 2, 4, 6, and 8%.
- (c) (i) Fe 0.3 + Ni 6%.
- (c) (ii) Fe 0.6 + Ni 12%.
- (c) (iii) Fe 1 + Ni 4%.
- (c) (iv) Fe 1.5 + Ni 2.5%.
- (c) (v) Fe 2.5 + Ni 4%.
- (c) (vi) Fe 3 + Ni 3%.
- (c) (vii) Fe 3.5 + Ni 2%.
- (c) (viii) Fe 4 + Ni 5%.
- (c) (ix) Fe 4.5 + Ni 0.5%.
- (c) (x) Fe 5 + Ni 2%.
- (d) (i) Mn 2 + Mg 2 and 2.5%.
- (d) (ii) Mn 2.5 + Mg 5%.
- (d) (iii) Mn 4 + Mg 1.5, 3, 3.5, 12, 14, and 18%.
- (d) (iv) Mn 6.5 + Mg 2%.
- (e) (i) Mg 1 + Cr 1, 3, and 5%.
- (e) (ii) Cr 1 + Mg 3 and 5%.

Quaternary Alloys

- (f) Cu 3.5 + Co 3 + Be 0.25, 0.5, 1, and 1.5%.

2. CHILL-CAST BARS OF ALLOYS CONTAINING NITRIDES

Early attempts to combine aluminium with nitrogen by passing the gas through the molten metal at various temperatures up to 1000° C. were not successful. In an effort to introduce nitrogen in combination with a second element, some experiments were made in which the gas was passed through the following binary alloys of aluminium: (a) chromium 2%, (b) magnesium 4 and 10%, (c) iron 2%, (d) titanium 1%, and (e) vanadium 2%. Melts of these binary alloys were covered with a mixture of sodium and potassium chlorides, and purified nitrogen was passed through an

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alumina tube into the molten metal at 900°–1000° C. for about 5 hr. After stirring, the melts were poured into a horizontal mould. The pouring temperature varied with the different alloying elements, and was in the range 730°–1000° C.

It was found that not more than 0.05–0.15% nitrogen combined during this treatment. Accordingly, alloys containing greater amounts of nitrogen were prepared by the powder method described below.

3. POWDER METHOD FOR PRODUCING ALLOYS CONTAINING NITRIDES

(i) Preparation of Nitrides

For the preparation of aluminium nitride, the most satisfactory technique was found to consist in heating superfine aluminium powder (Northern Aluminium Company's "Cyclone B") in an alumina boat in a stream of dry ammonia. During the reaction the temperature was raised from 600° to 1050° C. over a period of 8 hr. Material prepared by this means contained 90% AlN, the remainder being aluminium.

It was found that dry ammonia or oxygen-free nitrogen reacted with titanium powder quite readily at 1000° C. to give a yellow powder, containing about 73% TiN. Grinding the product, followed by re-treatment in ammonia, did not increase the proportion of nitride.

(ii) Sintering and Extrusion

An attempt to introduce a dispersion of nitride into the alloy by adding the powder to molten aluminium was unsuccessful. It was therefore decided to investigate the use of powder-metallurgy techniques in which the powders were compressed, sintered, and extruded hot.

Blown aluminium powder of about 120 mesh was used for preparing the alloys, and before mixing with nitrides and other ingredients the powder was freed from oxide with diluted orthophosphoric acid. The mixture was ball-milled for 24 hr. in an aluminium or mild-steel container, using steel balls and a xylene coolant; it was then filtered, washed with benzol followed by alcohol, and finally dried. The powder was cold pressed at 30 tons/in.² to form a compact 0.9 in. in dia. × 1 in. long. To prevent the powder from sticking, the steel die was lubricated with a suspension of colloidal graphite in acetone. After surface cracks had been removed with emery paper, the compact was sintered for 16 hr. at 500° C. in a mullite tube through which dry purified nitrogen was passed. The sample was then machined to give a disc $\frac{3}{4}$ in. in dia., which was heated to 450° C. and extruded to form a blank about $\frac{5}{16}$ in. in dia. × 6 in. long. The extrusion dies were pre-heated to 150° C. and were lubricated with a mixture of flaked graphite and petroleum jelly.

The materials made by the powder-extrusion method consisted of sintered bar made from aluminium powder, extruded, and binary alloys containing (nominally): (a) copper 4%, (b) nickel 5%, (c) TiN

2%, and (d) AlN 2%. The binary alloys of aluminium with copper or nickel were included so that the results obtained by using the powder-metallurgy technique might be compared with those obtained by casting.

4. METHODS OF TESTING

The values of Young's modulus were determined by the static method described in a previous paper,² and were reproducible to $\pm 0.5\%$.

III.—EXPERIMENTAL RESULTS

1. CHILL-CAST ALLOYS NOT CONTAINING NITROGEN

(a) Al-Co-Be Alloys

Results for the ternary aluminium-cobalt-beryllium alloys listed in Table I show that when the cobalt : beryllium ratio lies between 6 : 1 and 1 : 1, the increase in Young's modulus over that of chill-cast pure aluminium (9.5×10^6 lb./in.²) is greater than that calculated by adding together the known effects of cobalt and beryllium separately.

TABLE I.—Values of Young's Modulus for Chill-Cast Aluminium-Cobalt-Beryllium Alloys.

Chemical Composition		Young's Modulus, lb./in. ² × 10 ⁶	
Be, %	Co, %	Calculated	Observed
1.10	1.70	10.02	10.55
0.88	3.50	10.32	10.75
0.84	5.70	10.71	11.10
2.25	0.80	10.01	10.00
3.40	0.60	10.26	10.20

The microstructure of aluminium-cobalt-beryllium alloys polished electrolytically consisted of very fine aluminium-beryllium eutectic and Co₂Al₃. At higher beryllium contents, primary beryllium also separated. Fig. 1 (Plate LXVI) shows the structure of an alloy containing cobalt 0.80 and beryllium 2.25%.

(b) Al-Cu-Be Alloys

The results for ternary alloys with copper and beryllium (Table II) indicate that the observed values

TABLE II.—Values of Young's Modulus for Chill-Cast Aluminium-Copper-Beryllium Alloys.

Chemical Composition		Young's Modulus, lb./in. ² × 10 ⁶	
Be, %	Cu, %	Calculated	Observed
1.08	1.92	9.85	10.25
1.12	4.20	10.05	10.50
1.16	6.20	10.20	10.70
1.35	8.32	10.40	10.60

of Young's modulus are again greater than those obtained by calculation. This increase is attributed to the existence of a ternary Al-Cu-Be phase.

The structure of an alloy of aluminium with 8.32% copper and 1.35% beryllium is shown in Fig. 2 (Plate LXVI). Hexagonal particles of beryllium are present, together with aluminium-beryllium eutectic, CuAl_2 , and, associated with it, a ternary Al-Cu-Be complex.

(c) *Al-Fe-Ni Alloys*

The modulus value of aluminium-iron-nickel alloys proved interesting because of the formation of a ternary compound which, according to Mondolfo,³ is monoclinic, isomorphic with Co_2Al_9 , and has the composition FeNiAl_9 . This compound contains a larger number of aluminium atoms than either FeAl_3 or NiAl_3 , and the two metals in combination were therefore expected to be more effective than separately. This expectation is confirmed by the results collected in Table III. The figures show that an alloy containing nickel 4.17% and iron 2.32% has a Young's modulus 13% higher than that calculated by adding the known effects of nickel and iron when present separately.

TABLE III.—*Values of Young's Modulus for Chill-Cast Aluminium-Iron-Nickel Alloys.*

Chemical Composition		Young's Modulus, lb./in. ² × 10 ⁶	
Fe, %	Ni, %	Calculated	Observed
0.34	6.27	10.59	10.25
0.63	12.60	11.71	12.05
0.83	4.30	10.40	10.65
1.44	2.40	10.23	11.05
2.32	4.17	10.71	12.10
2.93	3.23	10.70	11.65
3.65	2.10	10.69	10.85
4.25	4.85	11.28	12.10
4.50	0.65	10.67	10.65
4.80	1.98	10.90	11.50

Fig. 3 (Plate LXVI) shows the structure of an aluminium alloy with nickel 3.23% and iron 2.93%. In the non-equilibrium conditions resulting from rapid cooling of a chill-cast bar, the NiAl_3 and FeNiAl_9 compounds separated in chain-like formations surrounded by colonies of fine ternary eutectic. On etching in caustic potash solution, followed by etching in a solution containing hydrofluoric, nitric, and hydrochloric acids recommended by Raynor and Pfeil,⁴ the ternary phase appeared blue and NiAl_3 brown.

(d) *Al-Mn-Mg Alloys*

The values of Young's modulus for ternary aluminium-manganese-magnesium alloys are given in Table IV. An alloy containing manganese 4% and magnesium 12.84% showed an increase in Young's modulus of 0.63×10^6 lb./in.², as compared with the calculated value on the basis of the separate contributions of these elements. The structure of this alloy is shown in Fig. 4 (Plate LXVI), in which MnAl_6 and Mg_2Al_3 are present with a ternary (Al-Mn-Mg) constituent in the form of needles. Wakeman and Raynor⁵ identified a

ternary compound— $T(\text{Mn-Mg})$ phase—whose composition corresponded approximately to $\text{MnMg}_2\text{Al}_{10}$.

TABLE IV.—*Values of Young's Modulus for Chill-Cast Aluminium-Manganese-Magnesium Alloys.*

Chemical Composition		Young's Modulus, lb./in. ² × 10 ⁶	
Mn, %	Mg, %	Calculated	Observed
1.92	2.03	10.00	10.40
2.09	2.41	10.00	10.35
2.46	4.76	9.95	10.35
4.21	1.49	10.80	10.75
3.78	2.79	10.50	10.35
4.46	3.69	10.70	10.65
4.00	12.84	9.90	10.50
4.09	14.12	9.66	10.30
3.65	17.67	9.29	9.95
6.44	1.79	11.55	11.30

(e) *Al-Cr-Mg Alloys*

As shown in Table V, the addition of chromium to aluminium-magnesium alloys results in an improvement in their elastic modulus. Erdmann-Jesnitzer⁶ identified a ternary compound in this system, and according to Wakeman and Raynor,⁵ this phase lies in

TABLE V.—*Values of Young's Modulus for Chill-Cast Aluminium-Chromium-Magnesium Alloys.*

Chemical Composition		Young's Modulus, lb./in. ² × 10 ⁶	
Mg, %	Cr, %	Calculated	Observed
0.65	4.40	11.10	11.25
0.78	3.35	10.70	11.00
0.99	1.03	9.80	10.40
3.07	1.18	9.70	10.15
5.06	1.26	9.65	10.10

the range of compositions $\text{Cr}_2\text{Mg}_3\text{Al}_{25}$ to $\text{Cr}_2\text{Mg}_{4.5}\text{Al}_{23}$, and probably belongs to the same group of ternary compounds as $T(\text{MnMg})$, with an electron : atom ratio of 2.37.

(f) *Al-Cu-Co-Be Alloys*

In Table VI are collected the results of tests on aluminium-copper-cobalt-beryllium alloys, in which

TABLE VI.—*Values of Young's Modulus for Chill-Cast Aluminium-Copper-Cobalt-Beryllium Alloys.*

Chemical Composition			Young's Modulus, lb./in. ² × 10 ⁶	
Cu, %	Co, %	Be, %	Calculated	Observed
3.66	2.70	0.12	10.30	10.85
3.62	2.63	0.25	10.32	11.08
3.73	2.61	0.82	10.44	10.90
3.73	2.71	1.28	10.54	10.80

the concentration of copper and cobalt was kept constant and that of beryllium was varied. The highest increment in Young's modulus was found in the alloy with a ratio of cobalt to beryllium of about

10 : 1, and was probably associated with a quaternary phase identified in the structure.

2. ALLOYS CONTAINING NITROGEN

(i) Chill-Cast Alloys

Table VII gives the results of tests on binary alloys of aluminium with chromium, magnesium, iron, titanium, and vanadium, containing also small amounts of combined nitrogen. The Kjeldahl method used for the determination of such small proportions of nitrogen is considered to be inaccurate, and the deviations in the results of the analysis might have been 20–30% from the true values. Although it is difficult to establish quantitatively the relationship between the nitrogen content and the values of Young's modulus, the results in Table VII indicate that even small additions of nitrides have a beneficial effect upon the elastic properties.

TABLE VII.—*Values of Young's Modulus for Chill-Cast Binary Alloys of Aluminium with Chromium, Magnesium, Iron, Titanium, or Vanadium, Containing Small Amounts of Combined Nitrogen.*

Chemical Composition						Young's Modulus, lb./in. ² × 10 ⁶	
Cr, %	Mg, %	Fe, %	Ti, %	V, %	Combined N, %	Calculated *	Observed
2.00	Of the order of :	0.15	10.25
...	4.22	0.01	9.20	10.65
...	10.20	0.025	8.80	10.05
...	...	1.88	0.030	9.90	9.70
...	1.02	...	0.10	9.85	10.25
...	1.03	...	0.10	9.85	10.40
...	1.95	0.05	9.85	10.40
...	0.05	10.10	10.70

* By adding known increases in Young's modulus for the metals only.

The microstructure of an alloy containing 1.02% titanium and 0.10% combined nitrogen is shown in Fig. 5 (Plate XLVI). The TiAl₃ constituent separated in plate or needle-like formations, whereas the TiN is seen forming colonies of very fine particles at the grain boundaries.

(ii) Sintered and Extruded Alloys

In Table VIII are given the values of Young's modulus for sintered and extruded bars in binary alloys containing nitrides of aluminium and titanium. The values for sintered and extruded bars in aluminium-copper and aluminium-nickel alloys are included for comparison. The results show that a substantial improvement in Young's modulus can be obtained by additions of titanium nitride or aluminium nitride. To allow for the effect of the small amount of aluminium oxide film present in the sintered alloys, the improvement in the value of Young's modulus due to the nitride or metal addition was based on the value of 9.8×10^6 lb./in.² obtained on pure aluminium sintered bar.

It can be calculated from the results that the increase in Young's modulus due to 1 wt.-% nitrogen was 0.95×10^6 lb./in.² when the nitrogen was added

as aluminium nitride and 1.40×10^6 lb./in.² when introduced as titanium nitride.

TABLE VIII.—*Values of Young's Modulus for Annealed Aluminium Alloys Containing Nitrides.*

Samples were annealed at 500° C. for 16 hr. and cooled in the furnace.

Chemical Composition				Young's Modulus, lb./in. ² × 10 ⁶	
Cu, %	Ni, %	AlN, %	TiN, % Ti, %	Observed	Due to Nitride
4	10.20	...
...	5	10.55	...
...	1.5	10.50	0.50
...	...	2	...	10.45	0.65

IV.—DISCUSSION

In order to compare the technological usefulness of different alloying elements in binary aluminium alloys, the values for the effect on the Young's modulus of 1 wt.-% of each addition are collected in Table IX.

TABLE IX.—*Effect on Young's Modulus of Addition to Aluminium of 1 wt.-% of Various Elements.*

Element	Increment in E for 1 wt.-% of Element, lb./in. ² × 10 ⁶	Element	Increment in E for 1 wt.-% of Element, lb./in. ² × 10 ⁶
Nitrogen (as TiN)	1.40	Cobalt	0.185
Nitrogen (as AlN)	0.95	Nickel	0.165
Chromium	0.47 *	Tungsten	0.125
Chromium	0.37 †	Silicon	0.105
Titanium	0.375	Copper	0.080
Manganese	0.34	Silver	0.075
Vanadium	0.32	Magnesium	−0.082
Molybdenum	0.30	Strontium	−0.20
Iron	0.23	Calcium	−0.30
Beryllium	0.19		

* Annealed alloys.

† As-cast alloys.

It was suggested in previous papers^{1,2} that the heat of formation of a compound should show a correlation with the elastic modulus. This suggestion was based on the fact that the compounds with a high heat of formation have tight bonding between atoms, and that therefore their elastic modulus should be high.

Oelsen and Middel,⁷ Kubaschewski and Walter,⁸ and Quill⁹ have given values for the heat of formation of the following intermetallic compounds :

Compound	Heat of Formation, kg.-cal./g.-atom
CuAl ₂	3.2
FeAl ₃	6.1
Co ₂ Al ₉	7.7
NiAl ₃	9.5
CaAl ₄	13.9
AlN	64.0
TiN	80.3

The values of Young's modulus for the alloys in which the above compounds are formed should increase in the same order as the heats of formation. The experiments have shown, however, that the presence of CaAl_4 in aluminium considerably reduces the elastic modulus, owing to the fact that this constituent has a layer structure which is known to possess a low value of Young's modulus.

In ternary systems, the data summarized in Table X show that the increment in Young's modulus relative to the separate effects of the added elements depends on whether or not a ternary compound is formed. Thus in the ternary alloys in group (1) of the table, no ternary compound is formed, and Young's modulus is determined by each binary phase acting independently. In group (2), with the exception of $\text{Cu}_2\text{Mn}_3\text{Al}_{10}$, the formation of a ternary phase reduces Young's modulus below the calculated value. This could be explained by the smaller proportion of aluminium in the ternary phase compared with the two respective binary phases.

TABLE X.—*Effect of Presence of Ternary Compounds on the Young's Modulus of Aluminium Alloys.*

Alloy Group	Aluminium Alloy with:	Intermetallic Compound		$E_{\text{calc.}} - E_{\text{obs.}}$ per 1 wt.-% $(A+B)$, lb./in. ² $\times 10^3$
		Binary $A_x\text{Al}_y, B_z\text{Al}_y$	Ternary $A_xB_z\text{Al}_y$	
(1)	Mn-Cr	$\text{MnAl}_6, \text{CrAl}_7$	None (in the chill-cast condition)	0
	Mg-Si	$\text{Mg}_2\text{Al}_3, \text{Mg}_2\text{Si}$	None	0
	Ni-Si	NiAl_3	"	0
	Cu-Cr	$\text{CuAl}_2, \text{CrAl}_7, \text{Cr}_2\text{Al}_{11}$	"	0
(2)	Cu-Mn	$\text{MnAl}_6, \text{CuAl}_2$	$\text{Cu}_2\text{Mn}_3\text{Al}_{10}$	0
	Mn-Si	MnAl_6	$\alpha(\text{AlMnSi})$; $\beta(\text{AlMnSi}) = (\text{MnSi})_2\text{Al}_3$ †	-0.033
	Fe-Si	FeAl_3	$\alpha(\text{AlFeSi}) = \text{Fe}_2\text{SiAl}_7$ (?); $\beta(\text{AlFeSi}) = \text{Fe}_3\text{Si}_2\text{Al}_9$ †	-0.055
	Cr-Si	$\text{CrAl}_7, \text{Cr}_2\text{Al}_{11}$	$\alpha(\text{AlCrSi}) = \text{CrSiAl}_3$ †; $\beta(\text{AlCrSi})$	-0.181
(3)	Mn-Mg	$\text{MnAl}_6, \text{Mg}_2\text{Al}_3$	$\text{MnMg}_2\text{Al}_{10}$	0.036
	Cr-Mg	$\text{CrAl}_7, \text{Mg}_2\text{Al}_3$	$\text{Cr}_2\text{Mg}_{14}\text{Al}_{23} - \text{Cr}_2\text{Mg}_3\text{Al}_{23}$	0.110
	Mn-Ni	$\text{MnAl}_6, \text{NiAl}_3, \text{NiAl}$	$X = \text{Ni}_4\text{Mn}_{11}\text{Al}_{60}$; Y	0.115
	Fe-Ni	$\text{FeAl}_3, \text{NiAl}_3$	FeNiAl_9	0.210
	Mn-Cr	$\text{MnAl}_6, \theta(\text{CrAl}_7 + \text{Mn})$	G = $(\text{MnCr})\text{Al}_{13}$ (in annealed condition)	0.237
	Cu-Be	CuAl_2	Identified. Ratio of Cu:Be favourable to $E \approx 2:1$; atomic composition not known	0.133
	Co-Be	Co_2Al_9	Not identified. Ratio of Co:Be favourable to $E \approx 2:1$	0.182
(4)	Cu-V	$\text{CuAl}_2, \text{VAl}_3, \text{VAl}_4$	Identified; atomic composition not known. Ratios favourable for E: Cu:V $\approx 6:1$; Cu:V $\approx 1:1$	0.076
				0.213

* The figures obtained on the alloys with the most favourable ratios of A to B.

† After Pratt and Raynor.¹⁰

The ternary alloys in group (3) are those having values of Young's modulus greater than the calculated values, because each ternary compound holds a greater proportion of aluminium atoms than the respective

binary compounds. Group (4) contains alloys in which ternary phases have been identified, though the quantitative compositions are not known. At certain compositions the value of Young's modulus is again appreciably higher than the calculated figure. It is believed that these intermediate ternary phases have a large proportion of aluminium.

To conclude, it is considered that the work described in this and previous papers provides sufficient information on which to base the development of a commercial aluminium alloy having elastic properties about 20% higher than those of the alloys at present in use. In fact, an alloy having a composition based on the aluminium-silicon eutectic, suggested by the author, has been produced on a large scale by Aluminium Laboratories, Ltd., and acknowledgement is made of their help in overcoming considerable difficulties encountered in the semi-continuous casting process. The material, rolled into sheet and fully heat-treated, gave values of Young's modulus of $11.8-12.0 \times 10^6$ lb./in.², which are very close to the predicted figure. The ultimate tensile strength of this alloy was of the order of 28 tons/in.², the 0.1% proof stress 21 tons/in.², and the elongation about 5%. When the material was aged at room temperature, the elongation increased to 10%; the proof stress, however, was reduced to 14.5 tons/in.², with the maximum strength lowered.

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REFERENCES

1. N. Dudzinski, J. R. Murray, B. W. Mott, and B. Chalmers, *J. Inst. Metals*, 1948, **74**, 291.
2. N. Dudzinski, *ibid.*, 1952-53, **81**, 49.
3. L. F. Mondolfo, "Metallography of Aluminium Alloys", p. 93. 1943: New York (John Wiley and Sons).
4. G. V. Raynor and P. C. L. Pfeil, *J. Inst. Metals*, 1947, **73**, 397.
5. D. W. Wakeman and G. V. Raynor, *ibid.*, 1948-49, **75**, 131.
6. F. Erdmann-Jesnitzner, *Aluminium Archiv*, 1940, (29).
7. W. Oelsen and W. Middel, *Mitt. K.-W. Inst. Eisenforschung*, 1937, **19**, 1.
8. O. Kubaschewski and A. Walter, *Z. Elektrochem.*, 1939, **45**, 630.
9. L. L. Quill, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics", p. 42. 1950: New York (McGraw-Hill Book Co., Inc.).
10. J. N. Pratt and G. V. Raynor, *J. Inst. Metals*, 1951, **79**, 211.

PLASTIC DEFORMATION OF ALUMINIUM-3.5% COPPER ALLOY SINGLE CRYSTALS *

1619

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SYNOPSIS

Long crystals of an aluminium-3.5% copper alloy, prepared by the strain-anneal method, have enabled a comparison to be made of specimens of identical orientation after different heat-treatments. Three conditions were investigated: (i) air-cooled from 535° C.; (ii) air-cooled and aged 3 days at 190° C.; (iii) air-cooled and overaged 2 days at 350° C., furnace-cooled to 250° C., held 1 day, and then furnace-cooled to room temperature.

Crystals of the air-cooled solid solution resembled pure metals, in so far as plastic deformation occurred on well-defined slip planes and the stress/strain curves were orientation-dependent. The deformation continued on the chosen system, suitably oriented alternative systems not becoming operative until heavy deformations were reached. In contrast, the fully hardened crystals did not show visible slip, nor did they undergo the change in shape expected from deformation on a single set of planes; furthermore, the stress/strain curves were independent of orientation. The behaviour of the overaged crystals fell between these two extremes.

The work-hardening of the aged and overaged crystals was greater than that of the solid-solution crystals, particularly when tested at -196° C. At room temperature the air-cooled solid-solution crystals, on interruption of the deformation, gave stepped stress/strain curves, which are explained in terms of accelerated ageing on the slip planes. Differences in the rate of work-hardening in the solid-solution and in the aged crystals are discussed in terms of the barriers which may prevent movement of dislocations.

I.—INTRODUCTION

WHILE much attention has been paid to the structural changes taking place in dilute aluminium-copper alloy crystals during ageing, their behaviour on plastic deformation has been comparatively neglected. Yet there is a definite need for information of this kind, as the emphasis of theoretical work on the strength of metals shifts from pure metals to alloys. Age-hardening alloys of the aluminium-copper type lend themselves to investigation, since simple heat-treatment can produce in them a variety of conditions, all of fundamental interest. Furthermore, structural studies on these alloys have reached a point where the changes that occur on ageing are known in considerable detail,¹ and this information should be of great value in the interpretation of the mechanical properties.

Karnop and Sachs² in 1928 investigated single crystals of an aluminium-5% copper alloy containing small amounts of silicon and iron, in two conditions: after quenching followed by ageing for 30 min. at 100° C., and after furnace-cooling to 300° C. No metallographic examination was made, the observations of greatest importance being the changes in cross-section of the crystals in the two conditions during deformation. There is clearly a need for a more detailed examination of alloy crystals of this type.

Recent work^{3,4} with pure-metal crystals had shown that orientation was a most important variable. With this in mind, it seemed very desirable to examine the effects of heat-treatment on crystals of identical orientation, so that any influence of orientation could be eliminated. In the present work, therefore, long single crystals were grown. These were subsequently cut into two or more specimens of identical orientation, which were then subjected to different heat-treatments or deformed at different temperatures.

II.—EXPERIMENTAL METHODS

1. CRYSTAL PREPARATION

The alloy was prepared from the purest material available, namely, 99.99% aluminium and spectroscopically pure copper, and contained 3.52 wt.-% copper. Melting was carried out in a small high-frequency induction furnace, using graphite crucibles. No impurities could be detected by normal chemical analysis. Small ingots, 1 × 1 × 7 in., were cast, rolled, and finally drawn through dies of square cross-section to produce long rods 0.135 in. square.

Single crystals were prepared from this material by the strain-anneal method. First the as-drawn rods were annealed for 5 min. at 560°–570° C. and air-cooled. The specimens were then strained by 1.0% elongation in tension, and placed in a travelling-tube

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gradient furnace, the hottest zone of which was maintained at 510°–520° C., the lowest temperature to bring about marked grain growth. The specimens passed into and through the hot zone at 0.65 cm./hr. This method produced crystals up to 12 in. in length, which were subsequently cut into two or more specimens. An alternative procedure involved heating the strained specimens slowly from 450° to 530° C. over 6 days in a stationary furnace, but no crystals more than 5 in. in length were obtained in this way.

2. MOUNTING

The crystals were prepared for mounting before the final heat-treatment. The two ends of the specimens were melted with an oxy-hydrogen flame into aluminium-alloy cups which surrounded them. These cups had been machined to fit into the standard split-steel collars of a Hounsfield tensometer.

3. HEAT-TREATMENT AND ELECTROPOLISHING

The mounted crystals were then subjected to the final heat-treatment, which always began with a solution-treatment of 16 hr. at 535° C., followed by air-cooling to room temperature. Such specimens formed the first set for examination. A fully hardened state (second condition for examination) was obtained by ageing for 3 days at 190° C., after which treatment the precipitate should possess the familiar θ' structure. A third condition, closely approaching equilibrium and designated "overaged", was also studied. This was reached by heating the air-cooled crystals for 2 days at 350° C., furnace-cooling to 250° C. where they were held for 1 day, and finally furnace-cooling to room temperature. In these specimens, the precipitate was the equilibrium CuAl_2 phase.

Finally, the crystals were electropolished in an ethyl alcohol/perchloric acid bath containing 100 ml. perchloric acid (sp. gr. 1.54) and 900 ml. ethyl alcohol, the voltage across the cell being 27–30.

4. TESTING

The crystals, after mounting, heat-treatment, and polishing, were deformed in a Hounsfield tensometer. Most of the experiments were conducted at room temperature, but some were carried out at -196°C . Crystals likely to age at room temperature were tested immediately after heat-treatment.

III.—EXPERIMENTAL RESULTS

1. AIR-COOLED CRYSTALS

(a) Method of Cooling

In preliminary experiments, the crystals, after solution-treatment, were water-quenched to keep the copper in solid solution. Unfortunately, this treatment set up internal stresses which led to plastic deformation of the crystals. Subsequent ageing at 300° C. for 30 min. caused precipitation on the

operative octahedral slip planes, showing that at least three planes had contributed to the accidental deformation (Fig. 1, Plate LXVII). On deliberate tensile deformation of these quenched crystals, instead of a single slip system operating, as predicted, several usually took part in the deformation, which was consequently very inhomogeneous. Fig. 2 (Plate LXVII) is a photomicrograph of a quenched crystal, extended 10%, in which the tension axis lay near the middle of the stereographic triangle, i.e. only one slip system should have operated.

It was thus necessary to adopt slower rates of cooling, and the later specimens were all air-cooled. Because of the small cross-section ($\frac{1}{8} \times \frac{1}{8}$ in.), this treatment resulted in a relatively rapid rate of cooling which allowed the development of almost the same degree of hardening on ageing as with the water-quenched crystals. The deformation of such crystals led to results which were more easily interpreted; Fig. 3 (Plate LXVII) shows a typical air-cooled crystal after 17% elongation.

(b) Stress/Strain Curves

Several crystals of different orientations (Fig. 9) were air-cooled, then immediately deformed at room

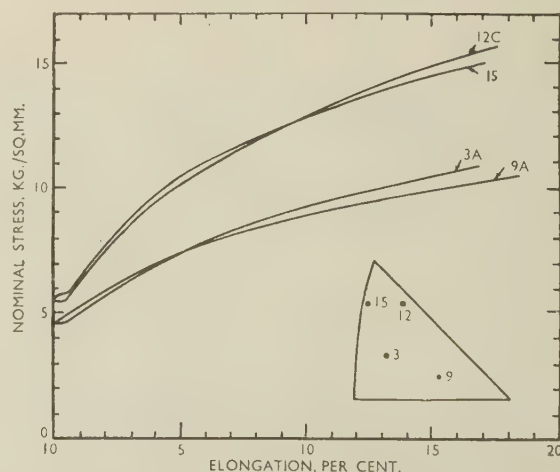


FIG. 9.—Stress/Strain Curves of Air-Cooled Al-3.5% Cu Single Crystals of Various Orientations.

temperature up to approximately 20% glide strain. Fig. 9 contains the stress/strain curves obtained. In the early stages of the deformation, a small, easy glide range was detected, except in the case of crystal 9A. An identical crystal (9B) tested later did show an easy glide range, suggesting that the first crystal may have been slightly deformed before straining.

On replotting the curves on a shear-stress/shear-strain basis, the differences between the several orientations became much less marked (Fig. 10). It thus appears that these crystals at least approximately obey the resolved-shear-stress law. The deviations are not as marked as for crystals of high-purity aluminium.³

(c) Micrographic and X-Ray Examination

Micrographic observations on the four crystals of Fig. 9 revealed well-defined slip on only one slip system, after elongations which would result in duplex slip in pure aluminium (Figs. 3-7, Plate LXVII). For

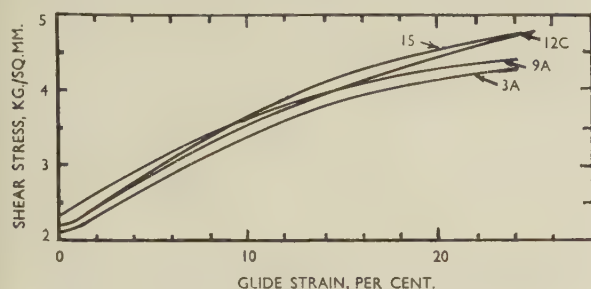


FIG. 10.—Shear-Stress/Shear-Strain Curves of Air-Cooled Al-3.5% Cu Single Crystals.

example, in crystal 15, which would be expected to deform by duplex slip at an early stage, a single slip system clearly predominates after 17% elongation. Figs. 3 and 4 illustrate the appearance of two adjacent faces at this stage; the latter shows some evidence of cross-slip. Even after 33% extension, only sporadic secondary slip was found (Fig. 6). Again, crystal 3A still slipped on one system after 50% extension (Fig. 5), although the [001]-[111] boundary was reached at less than 40% elongation. Very coarse slip bands usually appeared in the region of the neck just before fracture (Fig. 7).

Even after 55% extension, the spots in X-ray Laue photographs were sharp enough to permit accurate determination of the orientation. This suggests that if any inhomogeneities develop they are on a very small scale, a view confirmed by the microscopic observations. The lattice rotation observed was consistent with [110] being the slip direction; it was confirmed that considerable "overshooting" of the [001]-[111] boundary takes place.

2. FULLY HARDENED CRYSTALS

(a) Stress/Strain Curves

The tensile stress/strain curves for four crystals tested at room temperature are shown in Fig. 11. The points for three of the crystals fall almost on the same curve; the somewhat lower position of the curve for crystal 10A is attributed to a slight difference in the temperature at which ageing occurred. When the results of the four crystals were plotted on a resolved shear-stress/shear-strain basis, four widely different curves emerged, in contrast to the behaviour of the unaged crystals.

(b) Micrographic and X-Ray Examination

Electropolished crystals in the fully hardened condition showed no sign of precipitate on microscopic examination. In contrast, specimens accidentally deformed before ageing, e.g. in quenching, developed

striations; these specimens were not used in the experiments.

Microscopic examination after plastic extension revealed no trace of slip bands, except for some very coarse bands in the region of necking. This evidence, together with the wide scatter in the resolved shear-stress/shear-strain curves, suggests that the deformation cannot be described in terms of glide on one set of octahedral slip planes, as can be done for the unaged crystals. This view is confirmed by the observation that these crystals did not show the usual macroscopic rhombohedral distortion, but deformed in a manner similar to that of polycrystalline specimens, the square section not distorting appreciably.

X-ray Laue photographs taken after 4-5% deformation were somewhat blurred, but the more or less symmetrical distortion was not of the type usually associated with asterism. This suggests that the effect is associated with random lattice distortions on a very fine scale. X-ray micrographs taken by the

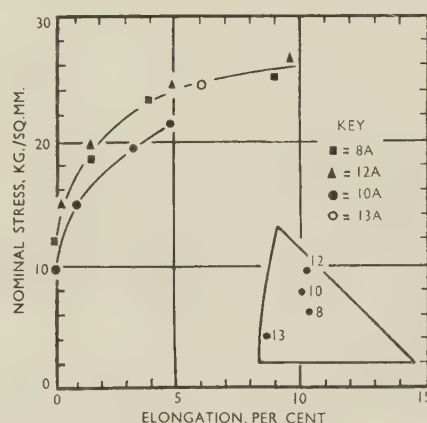


FIG. 11.—Stress/Strain Curves of Fully Hardened Al-3.5% Cu Single Crystals of Various Orientations.

Berg-Barrett technique revealed no deformation bands or other microscopic inhomogeneities.

3. OVERAGED CRYSTALS

(a) Stress/Strain Curves

Fig. 12 gives the stress/strain curves for crystals of four orientations. Crystals 8B, 10B, and 12B were tested at room temperature and had the same orientations as three specimens tested in the fully hardened condition (Fig. 11). Crystal 14A was tested at -196°C . The differences between the curves suggest some dependence on orientation, but because the rotation of the crystals during deformation could not be readily deduced from the blurred X-ray spots, the data were not plotted on a shear-stress/shear-strain basis.

These overaged crystals showed very low yield points, but the initial work-hardening was extremely rapid, approximating to that of the fully hardened crystals.

(b) Micrographic and X-Ray Examination

The microstructure of the overaged crystals comprised the depleted solid-solution matrix and CuAl_2 particles in the form of small rods or plates (Fig. 8, Plate XLVII). Up to about 10% deformation, slip

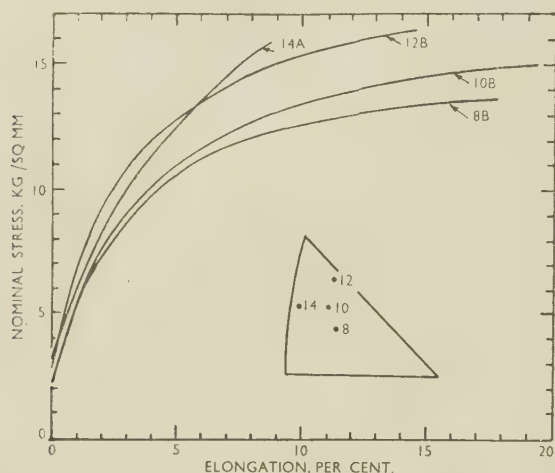


FIG. 12.—Stress/Strain Curves of Overaged Al-3.5% Cu Single Crystals of Various Orientations.

bands could not be detected, but after heavier deformations, fairly coarse slip bands were observed (Fig. 8) in some but not in all crystals.

X-ray Laue spots became blurred at an early stage of the deformation, to a greater extent than with the fully hardened crystals. Again X-ray micrographs did not reveal any inhomogeneities.

4. COMPARISON OF CRYSTALS IN DIFFERENT CONDITIONS

The use of identical orientations in the three different stages of ageing enabled a direct comparison of the

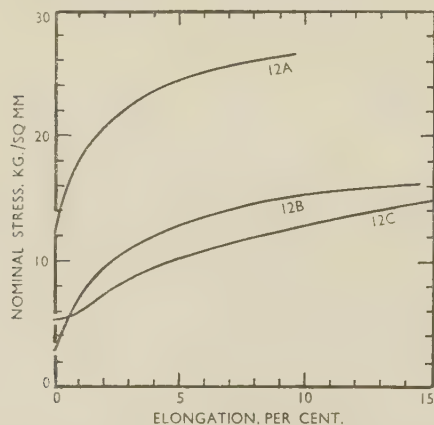


FIG. 13.—Showing the Effect of Heat-Treatment on the Stress/Strain Curves of Three Identically Oriented Crystals of Al-3.5% Cu in the Fully Aged (12A), Overaged (12B), and As-Air-Cooled (12C) Conditions.

effects of deformation to be made. In Fig. 13 are plotted stress/strain curves for three specimens from

crystal 12: 12A (fully hardened), 12B (overaged), and 12C (as-air-cooled). As expected, the fully hardened crystals possessed the highest yield stress, approximately four times that of the overaged crystals, whose yield stress in turn was about half that of the as-air-cooled crystals. The latter had the lowest rate of strain-hardening; most crystals in this condition gave a small region of easy glide. Both groups of aged crystals showed severe work-hardening and absence of easy glide. The rate of work-hardening appeared to depend only slightly on the distribution and nature of the second phase. The principal effect of the optimum ageing structure was on the yield strength.

5. YIELD-POINT PHENOMENA IN AIR-COOLED CRYSTALS

When the deformation of unaged air-cooled crystals at room temperature was interrupted, the yield stress on resumption of the test was appreciably higher, although the curve did not change its slope. This hardening took place within 10 min. at room temperature, and no great difference was apparent between

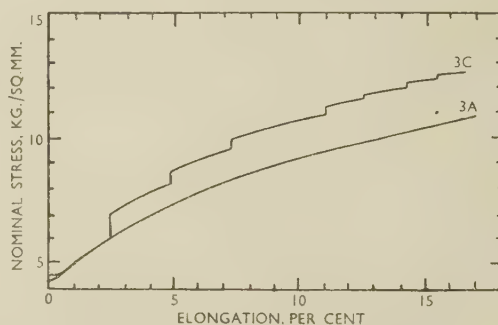


FIG. 14.—Stress/Strain Curves of Two Identical Air-Cooled Al-3.5% Cu Single Crystals. 3A continuously strained; 3C strained with interruptions of 15-min. periods.

the steps produced by this interruption and one lasting for 1 hr. It is thus evident that the steps do not arise from ordinary room-temperature ageing. A typical result is shown in Fig. 14, where two specimens from the same crystal were deformed, the one continuously, the other with a number of interruptions for a constant period of 15 min.

The effect of temperature was investigated for two different orientations, for each of which two identical crystals were available. In both experiments, one crystal was deformed at room temperature, and one in liquid nitrogen at the same strain rate. The curves obtained from one experiment are shown in Fig. 15. The crystals tested at -196°C . (9B) yielded at higher stresses, but the subsequent rate of hardening was so much smaller than that of the crystals deformed at room temperature (9A), that the curves crossed at an early stage of the deformation.

In contrast, the behaviour of two fully hardened crystals of identical orientation, one tested at room

temperature, the other in liquid nitrogen, is illustrated in Fig. 16. The yield stress of the crystal tested at -196°C . was the higher, and the stress/strain curve remained above that of the other crystal. In fact,

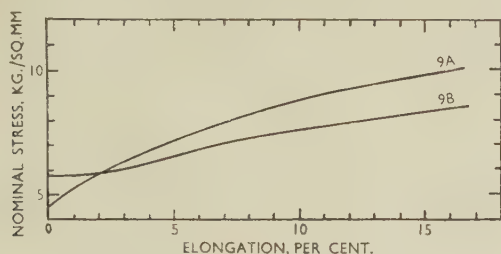


Fig. 15.—Showing the Effect of Temperature on the Stress/Strain Curves of Two Identical Air-Cooled Al-3.5% Cu Single Crystals. 9A deformed at room temperature; 9B deformed in liquid nitrogen (-196°C).

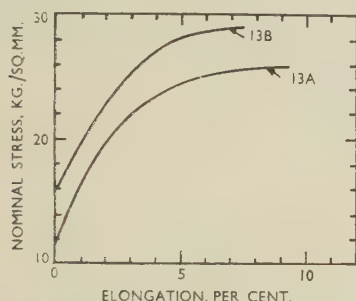


Fig. 16.—Showing the Effect of Temperature on the Stress/Strain Curves of Two Identical Fully Hardened Al-3.5% Cu Single Crystals. 13A deformed at room temperature; 13B deformed in liquid nitrogen (-196°C).

the rate of strain-hardening appeared to be almost independent of temperature within the range investigated.

IV.—DISCUSSION AND CONCLUSIONS

The experimental results obtained on aged crystals show that not only is the initiation of plastic deformation more difficult than in the case of the solid solution, but also work-hardening is more pronounced, particularly in the early stages of the deformation (Fig. 13). The stress at which plastic deformation begins depends very much on the ageing treatment; on the other hand, the rate of hardening during deformation does not appear to be very sensitive to structural changes resulting from ageing.

The high stresses at which fully hardened crystals yield have been explained by Mott and Nabarro⁵ in terms of the interaction of stress fields around the precipitate with dislocation lines. The lines are able to bend, but this is limited by the line tensions of the dislocations. In the fully hardened state the distance between particles is of the same order as the limiting radius of curvature of the dislocation, a condition resulting in maximum stability toward external stress. In overaged alloys, Orowan⁶ has suggested that the

more coarsely distributed particles can be by-passed by dislocation loops, which eventually join up, leaving dislocation rings around the particles. This model has recently been applied more generally by Fisher, Hart, and Pry.⁷ The present results cannot show whether either of these mechanisms operates, but they do indicate that in unaged alloys the deformation takes place almost exclusively on one set of planes, whereas in the aged alloys it is quasi-homogeneous.

The work-hardening behaviour of the air-cooled solid-solution crystals is very different from that of the aged crystals, resembling in some respects crystals of a pure metal, i.e., the stress/strain curves are orientation-dependent and the deformation occurs on well-defined slip planes. The strain-hardening of unaged crystals was very low, particularly at -196°C ., where complications due to ageing during deformation were avoided; at this temperature typical crystals showed an increase in the yield stress of barely 30% after 20% glide strain. This should be compared with the behaviour of 99.99% aluminium crystals at room temperature,³ where a glide strain of 20% results in a 500% increase in the yield stress. This striking difference may be closely connected with the tendency of the alloy crystals to deform on one glide system to the almost complete exclusion of other planes; whereas in pure metals, other systems take part in the deformation at a very early stage, resulting in a more pronounced hardening of the metal.

The fully hardened alloy crystals on the other hand, gave very similar stress/strain curves, irrespective of their orientations, and their change in shape during deformation was more akin to the behaviour of fine-grained polycrystalline aggregates. There was no visible slip, confirming the results of earlier work on polycrystalline aluminium alloys.^{8,9} It would thus appear that the deformation takes place by movement of relatively small groups of dislocations not confined to one set of planes. However, the exact mechanism of deformation cannot be decided until a full investigation is made by electron microscopy. These hardened crystals differ from those of pure metals in another respect, namely, that the rate of strain-hardening is not appreciably altered by lowering the temperature from room temperature to -196°C ., although the yield point is raised (Fig. 16). In the heat-treated crystals, the hardening is very probably due to the interaction of dislocations with particles of precipitate, the distribution of which is unaltered in the temperature ranges referred to. On the other hand, in pure metals the obstacles to slip, e.g. other slip bands, deformation bands, sub-boundaries, are more widely spaced, and their distribution is well known to depend on temperature, so it is not surprising that the strain-hardening is temperature-dependent.

The yield-stress phenomena encountered in the air-cooled solid-solution crystals bear a close resemblance to those found by Phillips¹⁰ in several polycrystalline aluminium alloys. Phillips considered that two phenomena gave rise to his stepped stress/strain curves: a transient increase in yield stress, which

disappeared on further deformation and which he attributed to locking of dislocations by solute atoms; and a permanent increase which raised the level of the whole stress/strain curve and which he considered to be an age-hardening process. In the present experiments, the evidence suggests that the steps observed are primarily the result of locally accelerated ageing on the active slip planes. Both the rate of straining and the temperature of deformation influence the shape of the stress/strain curve. The rate of straining has not been systematically investigated. Tests on identical crystals at room temperature and at -196°C . have shown that much less strain-hardening occurs at small deformations at the lower temperature. This supports the view that ageing is taking place during deformation at room temperature. In this connection it is significant that fully hardened crystals, which would not be expected to age-harden further during deformation, exhibit similar rates of hardening at room temperature and at -196°C .; the matter, however, requires further investigation.

ACKNOWLEDGEMENTS

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REFERENCES

1. H. K. Hardy and T. J. Heal, "Progress in Metal Physics", Vol. 5, p. 143. 1954: London (Pergamon Press).
2. R. Karnop and G. Sachs, *Z. Physik*, 1928, **49**, 480.
3. K. Lücke and H. Lange, *Z. Metallkunde*, 1952, **43**, 55.
4. F. D. Rosi, *Trans. Amer. Inst. Min. Met. Eng.*, 1954, **200**, 1009.
5. N. F. Mott and F. R. N. Nabarro, *Phys. Soc.: Conf. on Strength of Solids*, 1948, 1.
6. E. Orowan, *Inst. Metals: Symposium on Internal Stresses in Metals and Alloys*, 1948, 451 (discussion).
7. J. E. Fisher, E. W. Hart, and R. H. Pry, *Acta Met.*, 1953, **1**, 336.
8. G. C. Smith and D. W. Dewhurst, *Research*, 1949, **2**, 492.
9. C. Edeleanu, *J. Inst. Metals*, 1951-52, **80**, 187.
10. V. A. Phillips, *ibid.*, 1952-53, **81**, 649.

A THREE-DIMENSIONAL FACE-CENTRED CUBIC MODEL FOR THE STUDY OF CRYSTAL PHENOMENA *

1620

By P. R. ROWLAND,† M.Sc., Ph.D.

SYNOPSIS

The model, containing 10^3 – 10^4 lattice units, is rapidly and accurately assembled by pouring steel ball-bearings into a suitable transparent mould. Manipulation of the model has revealed a hitherto unsuspected lattice transformation, which results in the production of two new face-centred lattices bearing a twin relationship to each other but not to the original lattice. A corresponding transformation from face-centred cubic to close-packed hexagonal is also inferred. The model provides analogues of melting and annealing, and the effect of adding spheres of different sizes is described. In some cases these do not affect the lattice; nevertheless, only distortion-free, "solute"-free lattices undergo transformation without disruption, so that this affords a mechanism for the selection of portions having a perfect lattice.

Limited experiments using bubbles indicate that with elastic, cohesive spheres transformation may be initiated at a surface or other discontinuity and may proceed as a wave instead of by co-operative movement of the whole lattice, with consequent lowering of the activation energy required. Such transformations in a real crystal could involve blocks of only a few hundred atoms but, since these would have perfect lattices, interpretation of recrystallization data offers a possible means of investigating their existence.

I.—INTRODUCTION

IN the course of investigations into the chemical properties of the surfaces of copper single crystals,¹ it became necessary to find a method of preparing several different crystallographic planes as adjacent faces of an atomic model. If each face was to be of reasonable size (i.e. more than, say, four atoms in extent) the model had to contain a large number (of the order of 10^3 – 10^4) of units representing atoms. A difficult problem was thereby presented, in that this considerable number of spheres must be assembled into the face-centred cubic structure with reasonable accuracy. Steel ball-bearings were the obvious choice to represent the atomic units, because of the precision with which they are made, but it was not easy to stick them together with wax or adhesive without introducing inaccuracies due to varying thicknesses of cement between them. This difficulty was overcome by pouring ball-bearings into suitable transparent polyhedral moulds. It was then discovered that the models so formed could by manipulation be made to simulate phenomena occurring in real crystals, such as depression of the melting point by introduction of impurities, mechanical deformation, and, in particular, twinning of an unusual kind. It was felt that such models should find useful application in the study of crystal physics, and the methods of construction, together with the results of a preliminary survey of their properties, are therefore described below.

II.—CONSTRUCTION OF MODEL

1. RIGID MODEL

The mould is made by hinging together three equilateral glass triangles by means of adhesive cellulose tape to form three sides of a regular tetrahedron. The tetrahedron is held with the apex formed by the junction of the glass plates pointing downwards and the fourth side, that not covered with glass, uppermost and horizontal. When spheres are poured into this, they arrange themselves in close-packed planes parallel to the sloping walls. Consideration of the geometry of the situation shows that the interpenetrating "net-planes" so obtained form a face-centred cubic lattice, since the sides of a tetrahedron are parallel to the $\{111\}$ planes of a cube. The spheres are also automatically close-packed in the horizontal plane.

2. DEFORMABLE MODEL

In this case the mould is in the form of half a regular octahedron, that is, it consists of an inverted four-sided pyramid, the sloping sides being equilateral triangles of glass and the square base, which is uppermost and horizontal, being left open. Since the regular octahedron is derived from the regular tetrahedron by truncating each corner with a plane parallel to the opposite face, the sloping sides of this model also are parallel to the $\{111\}$ planes of a cube (Fig. 1). Again, the spheres arrange themselves in a

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face-centred cubic lattice, but in this case the uppermost plane is a cube face, $\{001\}$. As formed, this exhibits all the features to be expected on growing

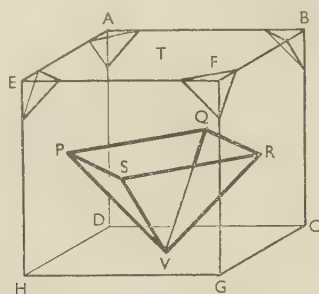


FIG. 1.—Diagram Showing Relation of Sides of the Model to the Planes of a Cube. $\{111\}$ planes have been cut out on the corners A, B, E , and F , to show that RSV is parallel to that at A , PSV is parallel to that at B , and so on.

crystal faces, such as steps with incomplete rows, vacant lattice sites, isolated atoms "adsorbed" on the surface, &c. Fig. 3 (Plate LXVIII) is a view of the model taken from opposite one of the glass triangles, i.e. looking upwards from a point below the model.

III.—PROPERTIES OF THE MODEL

1. TWINNING DEFORMATION

The model may be deformed by compressing a diagonal such as PR or QS (Fig. 1). The base $PQRS$, which is square when viewed from above, then takes on a diamond-shaped outline, although P, Q, R , and S are no longer in the same plane (Fig. 2). Deformation of this type does not lead to disruption of the lattice. Instead there is a smooth and continuous transformation into a bicrystal consisting

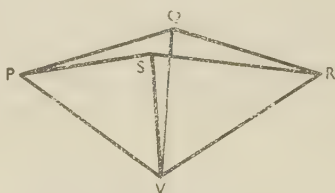


FIG. 2.—Diagram Illustrating Deformation of Model from Square to Diamond Shape.

of two halves, $PQSV$ and $RSQV$, each a regular tetrahedron with the face-centred cubic structure, the two halves being twinned on the composition plane QSV . Fig. 4 (Plate LXVIII) is a photograph of the model at this stage, taken from a point somewhat below the line QS .

When the model has reached the bicrystal state—where it virtually represents two rigid models fused back to back—it hardens sharply, further deformation requiring much greater force and resulting in disruption of the structure. It is convenient to make plaster moulds to hold the model, one for the original

and one for the bicrystal configuration, by fixing it in the required state with wire stays and pushing the apex into the plaster while this is still wet. This prevents the introduction of spurious effects through inadvertent wobbling of the glass plates. For the same reason the use of the rigid model may be desirable in such applications as those described in Sections 2 and 3 below.

Fig. 5 (Plate LXVIII) shows the top of the model with growth steps, &c., removed for photographic clarity, and it can be seen that the square arrangement of the atoms of the initial lattice has been transformed into a triangular pattern in each half of the bicrystal. At the same time, the whole plane is rotated out of the horizontal by $19\frac{1}{2}^\circ$, the directions of rotation being opposite for the two halves of the bicrystal. Throughout this transformation the planes of spheres originally parallel to the planes of SPQ and QRS remain parallel to them, respectively, as they rotate, and the same also holds for the net-planes parallel to the glass faces.

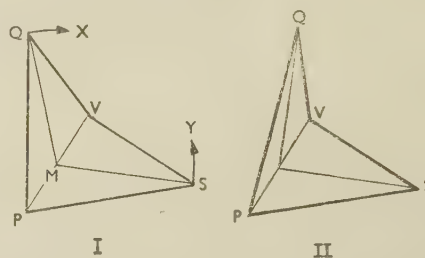


FIG. 7.—Diagram Illustrating Twinning Deformation of the Model.

The former change their type from $\{001\}$ to $\{111\}$ as they rotate, but the latter maintain the same symmetry throughout the transformation, being $\{111\}$ planes in both the initial and the final stages. Hence, there is no movement of the atoms relative to one another within these planes, and each plane glides as a whole over its next neighbour from the initial to the final stable position.

This is seen more clearly by considering one half of the bicrystal, $SPQV$, which in Fig. 7 (I) is shown lying on its side with the plane PSV horizontal. Twinning deformation of the model is then represented by rotation of Q towards S , as indicated by the line QX . The shearing movement is accompanied by a riding up of the planes concerned, and the demicrystal passes through a maximum of volume when the angle QMS is 90° (6% increase in volume), then subsides into the configuration of Fig. 7 (II). The same relative movement of spheres within the mould is obtained if the plane PQV is kept stationary and the leaf PSV is rotated as indicated by SY , so that planes parallel either to PQV or PSV may be regarded as shear planes according to convenience. Fig. 8 is a two-dimensional analogue, illustrating the process with rows of circles in place of planes of spheres.

Simple mechanical twinning in the face-centred

cubic lattice (which has never been observed in metals) would involve the same relative movement of planes. Thus, in simple mechanical twinning of the portion *SPQV* (Fig. 7) a $\{111\}$ plane such as *PSV* would remain stationary and become the plane of composition with the original lattice, the other planes moving parallel to it. On the other hand, the composition plane in the twinned model (*SQV*) is that which was initially $\{100\}$ and it only becomes $\{111\}$ through the transformation. Furthermore, the movement of the atomic planes during the transformation is not parallel to this plane.

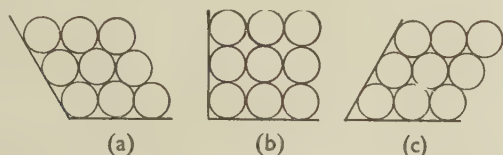


FIG. 8.—Two-Dimensional Analogue Illustrating Twinning Deformation.

The result of the transformation is a change of crystal axes for each half of the bicrystal. Thus, the direction *PR*, which was $[001]$ in the original model, becomes the common $[111]$ of the derived bicrystal and *SQ* changes type from $\langle 001 \rangle$ to $\langle 011 \rangle$ in each demicrystal. The vertical *VT* (Fig. 1) changes from type $[001]$ to $[11\bar{2}]$ and $[\bar{1}\bar{1}2]$, respectively (the direction *PR* being taken as positive for each). Transformations which convert the line *PR* from $\langle 001 \rangle$ to $\langle 111 \rangle$ in this way will be referred to as I-II-type and those in the reverse direction as II-I-type.

It should perhaps be pointed out that the model, if regarded solely as a type of calculating machine, yields only the information that two transformations are spatially possible, these being identical in all respects except that they are in a mirror-image relationship. From a mathematical point of view, the glass plates represent only geometrical constructions which aid calculation, and it is sometimes convenient to imagine the spheres as floating in gravitation-free space and held together by attractive forces, so that a model can possess a quite arbitrary external shape instead of forming part of an octahedron. The I-II-type transformation corresponding to one or other half of the bicrystal then appears as a uniform compressive strain along an initially $[100]$ direction, accompanied by a uniform extension along a line of spheres originally $[010]$ or $[001]$, which rotates through $19\frac{1}{2}^\circ$ as it extends in the plane which is initially (100) . Thus, a block which starts with plane faces always ends as a block with plane faces, although their dimensions and the angles between them will be changed. Such a block can equally well transform into an untwinned lattice or into two twinned blocks in four different ways. (Either the initial (010) or the (001) plane can become the final composition plane, and in each case rotation through $19\frac{1}{2}^\circ$ can take place in one of two different ways.) In the model itself the particular mode—division into two equal twins—

is determined by the constraints imposed by the glass plates, but it is readily conceivable that under other types of constraint a cubic block might, for example, be transformed into a series of twinned lamellae. The ultimate case would be that in which the twin boundaries were as closely spaced as possible, and the result would then be a close-packed hexagonal lattice with its *c*-axis along the $[010]$ or $[001]$ direction of the original, whichever was normal to the lamellae.

When handling the deformable model the positions of minimum energy (i.e. when the spheres are in the face-centred cubic arrangement) are felt as slight though definite “clicks”, but transformations between these positions, i.e. to or from the twinned state, are smooth and easy, suggesting that similar phenomena might be expected in face-centred cubic metals. In considering this possibility, two main points must be borne in mind. The first is that mechanical twinning by simple homogeneous shear, such as that occurring in each half of the bicrystal, as explained when discussing Fig. 7, is not known on a macroscopic scale.² The second is that the changes in shape of the blocks of material concerned could be accommodated by the surrounding matrix without setting up large stresses only if these blocks were small. Hence examples, if they occur, would probably be on a submicroscopic scale, and direct observation of them would be unlikely. The possibility is under consideration that such processes might play a part in the production of the deformation textures of face-centred metals and in the formation of annealing-twin nuclei. The latter are of particular interest because the transformation constitutes a selection mechanism for portions of perfect lattice, distorted lattices being disrupted when deformed in this way (see Section 2, below).

2. LATTICE DISTORTIONS

A distorted lattice may be produced either by rapid pouring of the spheres when the model is formed or by the introduction of spheres differing in size from those of the model. The distortions so generated cannot, strictly speaking, be regarded as analogues of dislocations, since, unlike the case of the bubble-raft,³ the spheres representing the atoms are not deformable; but their presence in any particular case gives an indication of the conditions under which dislocations might occur. Such distortions consist of misalignment of part of the lattice with an adjacent part. Distortions produced by rapid pouring may be removed by shaking the mould, which causes the misalignment boundaries to migrate through the model by transfer of atoms from one side of a boundary to another, the boundaries finally disappearing at the surface or by mutual annihilation. This, of course, is the analogue of annealing.

When spheres representing “solute” atoms, larger than those forming the model (the “solvent”) are introduced, each generally distorts the lattice over a considerable region. This is not an invariable rule,

however, and after "annealing" the model by shaking, the amount of disturbance in the region of such a sphere is sometimes found to be negligible. This appears to be due to the fact that the sphere accumulates lattice vacancies around itself in such a way that, together with its attendant holes, it occupies an exact number of lattice sites. Fig. 6 (a) (Plate LXVIII) shows such a sphere and surrounding lattice photographed through one of the glass sides of the model. Nevertheless, slight deformation of a model in this state by compression along a diagonal such as SQ (Fig. 1), as described above, causes misalignments to appear, emanating from the region of the larger atom (Fig. 6 (b), Plate LXVIII). Hence, a "solute" atom may have little distorting effect on the surrounding lattice and yet influence its mechanical properties.

A "solute" atom smaller than those comprising the model has rather less effect on the surrounding lattice, since vacant lattice sites frequently occur in models without disturbing the lattice, even when it is twinned, and a smaller sphere simply "rattles" within the boundaries of a lattice hole. However, if two or more such spheres in a model approach within one or two lattice spacings of each other, some of the intervening "solvent" spheres are no longer supported by firm contact with neighbours, and the lattice in that region tends to collapse. Hence, small atoms can interact with each other and give rise to lattice distortions. This effect is seen in operation when $\frac{1}{8}$ -in.-dia. "solvent" spheres are progressively added to somewhat smaller "solute" spheres ($\frac{7}{16}$ -in. or $\frac{3}{16}$ -in.-dia., 12 in number). When the "solvent": "solute" ratio is 1:1 it is not possible to form a lattice, and this remains the case until the ratio reaches the region of 7:1. (No superlattice formation was observed at the expected ratios in this or subsequent experiments.) At this point the tendency to lattice formation seems to set in fairly sharply, although the model so produced is highly distorted. As the ratio is further increased, the resulting lattices approach more closely to the ideal. The number of "solute" spheres in the surfaces (top and sides) of such models is higher than would be predicted from probability considerations, and they frequently appear in groups of two or three, so that it would seem that chance encounters result in distortions which are partially eliminated by diffusion to the surface of the groups of "solute" atoms, together with their surrounding misalignments. As more "solvent" atoms are added, the tendency for "solute" atoms to appear preferentially in the surface diminishes, presumably because the model is made bigger and so the volume:surface ratio increases. When the "solvent": "solute" ratio reaches 20:1, the lattices obtained appear fairly uniform, but even at 100:1 disturbances are seen when the model is twinned.

When the "solute" spheres are larger than those of the "solvent" ($\frac{5}{16}$ -in.-dia., 12 in number) the ratio at which a lattice can form is again 7:1 or 8:1, but the tendency to segregation at the surface of the model is much smaller, most of the "solute" atoms re-

maining within the lattice. Since the majority of these positively distort the lattice, the latter departs visibly from the ideal until a rather higher "solvent": "solute" ratio is reached than in the case of smaller "solute" spheres. The lattice disturbances arising when the model is deformed are at all times greater with the larger "atoms" and are clearly observable at a ratio of 250:1.

3. MELTING

When a model containing "foreign" atoms is shaken with gradually increasing intensity, parts of the surface become mobile before the main part of it "melts". These lie over the regions which are distorted by the "foreign" spheres and the process is an analogue of the lowering of the melting point of a solid by the introduction of impurities. When "pure" models are shaken so that the spheres become mobile, they show a marked tendency to set suddenly into a lattice at a certain point as the intensity of the agitation is decreased, but when "foreign" spheres are present in appreciable numbers, this sharpness is lost. The binding energy of the model is, of course, derived from a type of field very different from that holding a crystal together, the one originating from gravity acting via inclined planes and the other from chemical bonding, and the binding of a sphere within the model increases with its depth below the surface. However, melting is a surface phenomenon, and since only the top layers are involved in the experiment, the analogy is a reasonably good one. Localized "melting" of the surface in this way is a useful means of detecting a "foreign" sphere which has become lost in a large model, and so is the appearance of disturbances when the model is twinned.

IV.—BUBBLE MODELS

The value of the models would be greatly enhanced if they could be made of elastic, cohesive spheres, as in the case of the bubble-raft model, and many attempts were made to form three-dimensional bubble models. Two main difficulties were encountered: (i) finding a suitable method for separation of the bubbles from the surface of the liquid on which they were prepared, and (ii) fragility and even spontaneous collapse of the bubbles, due to the fact that when removed from an aqueous surface they drained and thinned rapidly. Among methods tried were preparation of inverted models underwater in air-tight moulds, "pipe-lining" bubbles from their point of emergence on the surface in tubes of suitably calculated cross-section, &c., but the products were too ephemeral to permit of careful study. However, one observation of possible significance was recorded, namely, that an exposed {001} surface appeared to be unstable, localized groups of atoms tending to become close-packed, i.e. to pass over into type {111}. This suggests an interesting theoretical model in which a I-II-type transformation, instead

of taking place by an all-at-once process, as in the ball-bearing model, might be initiated at a {001} surface and proceed by passage of a wave of transformation, with part of the lattice already transformed and part in its initial state, the two joined by a moving portion containing layers in various intermediate states. The direction of the wave would be along $\langle 001 \rangle$ of the original crystal. Such a process is somewhat analogous to movement of a dislocation, and would require only the energy associated with the transition portion, instead of that for the 6% total volume expansion of the all-at-once process.

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REFERENCES

1. P. R. Rowland, *Nature*, 1949, **164**, 1091.
2. R. Clark and G. B. Craig, "Progress in Metal Physics", Vol. 3, p. 128. 1952: London (Pergamon Press).
3. W. L. Bragg and J. F. Nye, *Proc. Roy. Soc.*, 1947, [A], **190**, 474.

1621 TENSILE PROPERTIES OF SOME TITANIUM ALPHA SOLID SOLUTIONS UP TO 600° C.*

By J. W. SUITER,† M.Sc., STUDENT MEMBER

SYNOPSIS

The ultimate tensile stress and elongation to fracture have been measured for two series of binary titanium alloys, one containing nitrogen, oxygen, or carbon; the other containing aluminium, tin, or zirconium.

Up to 300° C. the strength decreases rapidly with increasing temperature. This effect is most marked in the alloys containing oxygen, nitrogen, and carbon. In the range 350°–500° C., the strength remains approximately constant, but above 500° C. it again falls rapidly. Accompanying changes are found in the elongation to fracture.

An explanation of this behaviour is given in terms of the "atmospheres" of oxygen, nitrogen, or carbon atoms around dislocations. The addition of aluminium, tin, or zirconium tends to overcome the effects of the interstitial impurities and leads to superior properties up to 600° C.

I.—INTRODUCTION

THE most recently developed alloys of titanium for applications at high temperatures have been of the single-phase type, based on the solid solution of aluminium in α -titanium.^{1,2} Development of this class of alloy has been rendered necessary by the structural instability, at moderate temperatures, of the β phase in titanium alloys, unless large alloying additions are made. This instability of the β phase may lead to accelerated creep during the course of the transformation, or it may result in embrittlement when the alloy cools to room temperature.

In the present work, the tensile properties of various solid solutions based on α -titanium, have been measured at temperatures up to 600° C. Two classes of alloying addition were made:

(a) Elements which form interstitial solid solutions (oxygen, nitrogen, and carbon).

(b) Elements which form substitutional solid solutions (aluminium, zirconium, and tin).

With the exception of carbon, all these elements have appreciable solid solubility in α -titanium.

II.—EXPERIMENTAL PROCEDURE

1. MATERIALS

The titanium, produced by the Kroll process, which formed the basis material for the alloys, contained as main impurities: oxygen 0.5, nitrogen 0.2, carbon 0.1, iron 0.15, and magnesium 0.15 at.-%. Metallic alloying additions were made from high-purity aluminium (99.99%), high-purity tin (99.9%), and Kroll zirconium (99.3% Zr + Hf). Pigment-grade titanium dioxide, gaseous nitrogen, and high-purity carbon were added to form the other alloys.

2. PREPARATION OF THE SPECIMENS

The titanium was first melted in a Kroll-type arc furnace and the alloying additions were then made to give ingots of some 40–50 g. An elaborate procedure of remelting was adopted to ensure that the ingots were homogeneous. The weight loss during alloying was generally less than 0.2 g., and when this was small in comparison with the weight of the addition, the nominal composition was accepted as the actual composition. In other cases the alloys were analysed, and the agreement between nominal and actual composition was found to be good.

Ingots were swaged in the range 700°–800° C. to form bars $\frac{1}{4}$ in. in dia. Macro-etching and hardness tests on sections along the bar indicated the absence of inhomogeneity in all cases. From the rod, miniature specimens with a gauge-length of $\frac{3}{4}$ in. and a dia. of $\frac{1}{8}$ in. were turned on a lathe. Before testing, all specimens were annealed for 3 hr. at 750° C. in a vacuum at a pressure of 10^{-5} mm. of mercury. After this treatment all alloys showed a uniform structure consisting entirely of α solid solution, with grain-sizes in the range 1000–2500 grains/mm.,² depending on the alloy content.

3. TESTING PROCEDURE

The testing was carried out at a constant strain rate (1.5%/min.) in an electrically operated machine similar to that described by Manjoine.³ In plotting stress/strain curves, the movement of the cross-head was taken as the elongation; this procedure leads to some error, which was reflected chiefly in the value of Young's modulus. The elongation to fracture was later measured from gauge marks on the specimen.

Specimens were held at the testing temperature for 3 hr. before straining. Although the tests were conducted in air, even at the highest temperature (600° C.)

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only thin adherent oxide films were formed on the specimens. The temperature during a test was controlled to $\pm 2^\circ\text{C}$., and the maximum variation along the gauge-length was about 3°C . Comparison between the thermocouple normally used for temperature measurement and one spot-welded to the gauge-length of a specimen, confirmed that a correct value of the specimen temperature was obtained.

Repeat tests on specimens cut from the same ingot and also from other ingots of the same nominal composition revealed good reproducibility. Tensile-stress values had a scatter of about 4000 lb./in.² at the lower temperatures, but this decreased to about 2000 lb./in.² at 600° C. Values of elongation to fracture showed a scatter of about 3% strain at temperatures up to 500° C. and about 20% strain at 600° C.

III.—RESULTS

1. INTERSTITIAL ALLOYS CONTAINING NITROGEN, OXYGEN, OR CARBON

Figs. 1 (a) and (b) show the curves for ultimate tensile stress and elongation to fracture as a function of temperature, for the basis titanium (0.2 at.-% nitrogen) and two nitrogen-containing alloys. The most striking feature is the small hardening effect of nitrogen at high temperatures compared with that at room temperature; for example the alloy with 1.6 at.-% nitrogen has a U.T.S. value at room temperature about 50,000 lb./in.² greater than that of the 0.2 at.-% nitrogen alloy, but at 600° C. the difference is reduced to 4000 lb./in.².

These curves may be divided into three temperature ranges: (i) Up to 300° C., the strength falls off very rapidly and the elongation to fracture increases; (ii) from 350° to 500° C., the strength remains almost constant and the elongation to fracture decreases; (iii) at still higher temperatures, the strength again falls rapidly and the elongation to fracture increases markedly. Associated with these three ranges of temperature are changes in the shape of the stress/strain curves, which follow the same pattern as those found by Rosi and Perkins⁴ for commercial titanium. Below 300° C. the stress/strain curves exhibit a yield point, but at higher temperatures this disappears. Above 500° C. the stress, after reaching a maximum, falls in a series of steps; if an approximate correction, derived from the cross-head movement, is made for the reduction in area, then these steps become a series of serrations for which the mean stress is approximately constant.

Changes in ductility can easily be seen from the nature of the fractured specimens of the 0.9 at.-% nitrogen alloy (Fig. 8, Plate LXIX). Below 300° C. the specimen sustains a fairly large overall elongation, yet the actual fracture appears to be of the brittle type. At 400° C., and to an even greater extent at 500° C., the overall elongation decreases and most of the deformation occurs locally near the fracture. At

600° C. the specimen is extremely ductile, the whole gauge-length being drawn down to a very fine point. The variation in nitrogen content from 0.2 to 1.6 at.-% apparently has no effect on the temperature ranges in which these effects are found.

Similar results were obtained for the series of oxygen and carbon alloys, the curves for which are given in Figs. 2 and 3, respectively. These show temperature ranges similar to those found with the nitrogen alloys, and again these are independent of the amount of added element.

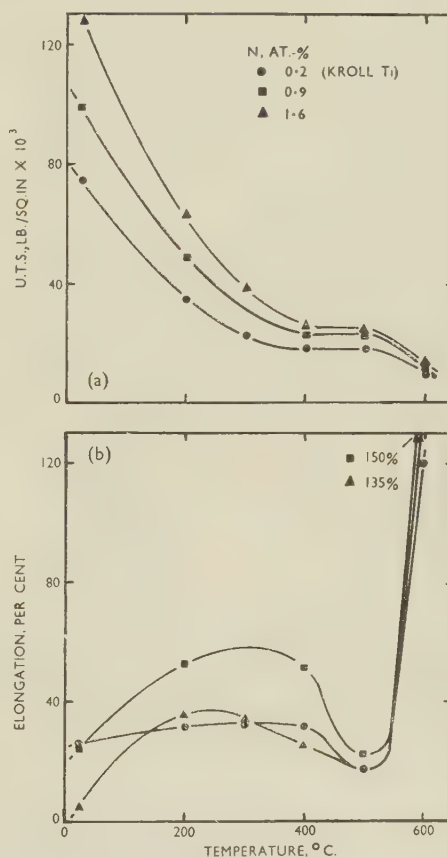


FIG. 1 (a) and (b).—The Effect of Nitrogen on the Mechanical Properties of Titanium.

As mentioned later, it was thought that the interstitial impurities might be the cause of these effects. A series of tests was therefore conducted on iodide-refined titanium, which was considerably purer than the Kroll material. As shown by Fig. 4, the curves for the iodide titanium were similar to those for the Kroll material, but displaced in a manner consistent with the reduced oxygen and nitrogen content.

2. SUBSTITUTIONAL ALLOYS CONTAINING ALUMINIUM, ZIRCONIUM, OR TIN

The ultimate tensile stress and elongation to fracture for a series of aluminium alloys are shown in Figs. 5 (a) and (b) as functions of the test temperature. These

curves may again be divided into three ranges, and, as in the case of interstitial alloys, the temperature ranges appear to be independent of the amount of added element. An important point is that the decrease in strength in the range 0°–300° C. becomes less the higher the aluminium content, so that up to some 500° C. these alloys retain a much greater proportion of their room-temperature strength than do

was noted that alloys containing more than 6 at.-% tin, failed in an intercrystalline manner above 500° C., with low values of elongation to fracture.

The results for the zirconium alloys (Fig. 7) exhibit a new feature. Here the temperature ranges, previously found to be independent of composition, are displaced to lower temperatures with increasing zirconium content. Thus, the intermediate temper-

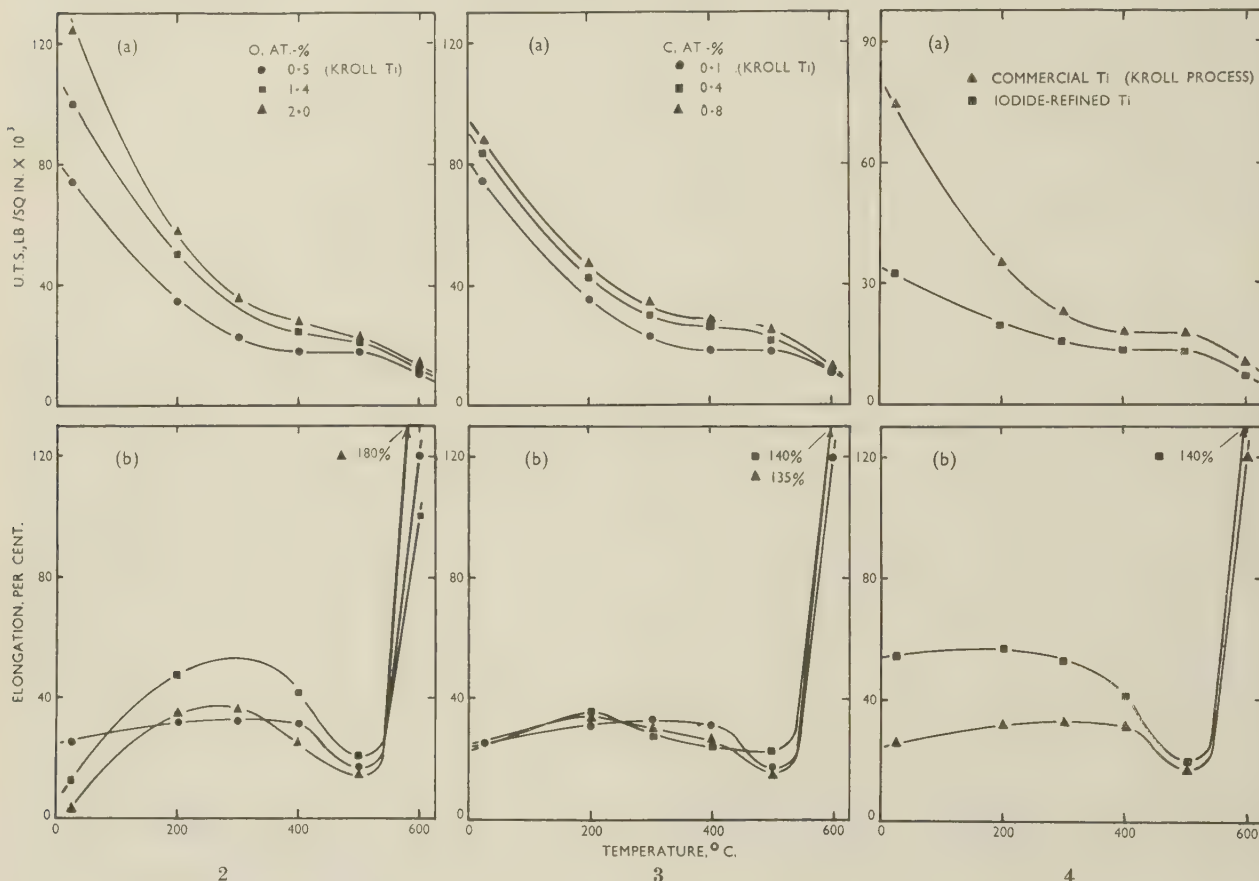


FIG. 2 (a) and (b).—The Effect of Oxygen on the Mechanical Properties of Titanium.
FIG. 3 (a) and (b).—The Effect of Carbon on the Mechanical Properties of Titanium.
FIG. 4 (a) and (b).—The Effect of Impurities on the Mechanical Properties of Titanium.

the interstitial solid solutions. Over the same temperature range the elongation to fracture remains essentially constant. However, the strength decreases rapidly above 500° C.

The results for the tin-containing alloys, reproduced in Fig. 6, follow the same trend as those previously studied. The decreases in the first and third temperature ranges are more marked than with the aluminium alloys, but not so marked as in the case of the interstitial alloys. This leads to inferior properties; for example, the properties at room temperature of the 6 at.-% tin and the 12 at.-% aluminium alloys are almost identical, but at 500° C. the difference in U.T.S. is 12,000 lb./in.² and at 600° C., 20,000 lb./in.². It

ature range, where the strength is approximately independent of the temperature, is depressed by about 100° C. by the addition of 12 at.-% zirconium.

IV.—DISCUSSION

The ultimate-tensile-stress/temperature curves, for all the alloys studied, may be divided into three parts:

(1) Up to 300° C. the strength falls off rapidly. This decrease is more marked in the case of interstitial solid solutions than in that of substitutional solid solutions.

(2) In the range 350°–500° C. the strength is approximately independent of the temperature.

(3) Above 500° C. the strength again falls off rapidly.

At present no definite explanation of the properties of these titanium alloys can be put forward. Two hypotheses were examined, but both contained inconsistencies in detail. Rosi and Perkins⁴ have suggested that strain-ageing occurs in commercial titanium as it is strained in the range 300°–500° C. and that oxygen,

cause strain-ageing effects. Although the effects were still found in iodide titanium containing only 0.03 at.-% nitrogen, it can be seen that in the case of Kroll titanium the effects were more marked the higher the interstitial alloying content. This content differs by an order of magnitude from the carbon content necessary to produce strain-ageing in steel, however, some difference might be expected because of the much

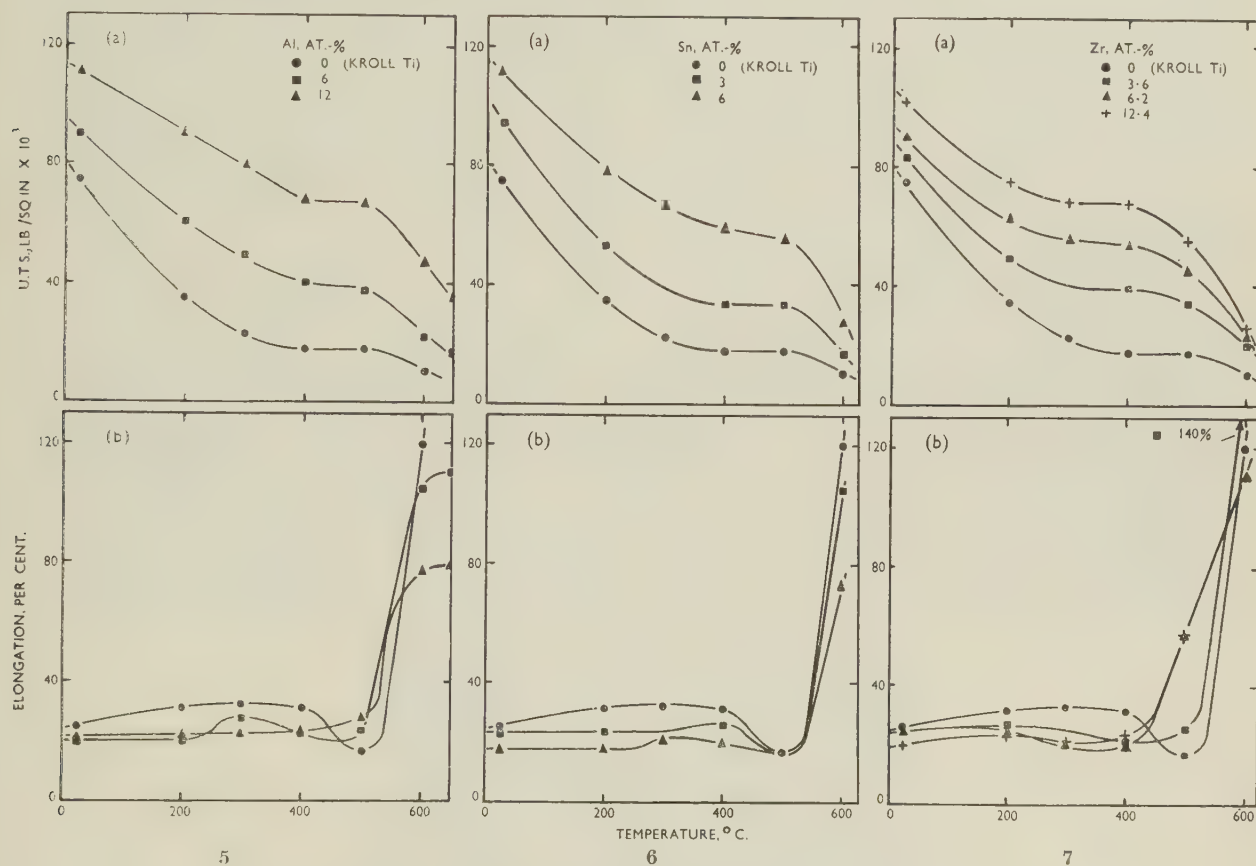


FIG. 5 (a) and (b).—The Effect of Aluminium on the Mechanical Properties of Titanium.

FIG. 6 (a) and (b).—The Effect of Tin on the Mechanical Properties of Titanium.

FIG. 7 (a) and (b).—The Effect of Zirconium on the Mechanical Properties of Titanium.

nitrogen, or carbon might be responsible for this behaviour. It is interesting to note that Pratt, Bratina, and Chalmers⁵ deduced from internal-friction measurements that movements of oxygen atoms occurred at a peak temperature of 450° C. This is approximately in the middle of the postulated strain-ageing range, where the strength is essentially independent of the temperature. Two difficulties arise from the strain-ageing concept, however. First, strain-ageing is generally considered to affect only the yield properties. However, as Rosi and Perkins have shown, the yield strength of titanium is very close to its ultimate tensile stress and closely follows it in its variation with temperature. The second difficulty lies in the amount of interstitial element necessary to

greater solubility of oxygen and nitrogen in titanium.

On the basis of the ideas outlined above, it is possible to suggest that the effect of addition of elements which form substitutional solid solutions will differ from that of elements which form interstitial solid solutions, since it appears unlikely that two distinct types of hardening will have the same temperature-dependence. Some preliminary experiments on ternary alloys containing aluminium and oxygen show that oxygen can render the effects still more pronounced, even though hardening due to other causes is present. To explain the effect of zirconium, it must be assumed that increasing the amount of it permits greater freedom of movement of the interstitial atoms through the lattice.

From the practical point of view, two lines of attack are open if the above ideas are correct. First, it would appear beneficial to remove the impurities and to induce hardening by other means less dependent on temperature. Secondly, it might be possible to make alloying additions which would decrease the freedom of movement of the interstitial atoms and so delay to higher temperatures the final decrease in strength. At present there is no indication which additions would bring this about.

Recently, M. K. McQuillan⁶ has suggested that changes occur in the electronic structure of titanium "some hundreds of degrees" below the transformation temperature. If this is so, then variations in atomic bonding and in strength might be expected in this temperature range, and could account for the present results. This idea might also explain why zirconium depresses the temperature at which the effects occur. However, it is not easy to see why additions of aluminium, which raises the transformation temperature, have no effect on the temperature ranges. Moreover, the difference between substitutional and interstitial solid solutions is not explained. It should be possible to distinguish between the two possible mechanisms, for if the observed effects arise from electronic changes then they should still be obtained in pure titanium, while if strain-ageing is the cause, then the effects should not be present in that material.

One further line of enquiry now being followed in

this laboratory is that changes in strength and ductility may be associated with alterations in the mechanism of deformation. Because of the superficial oxidation of the specimens, no evidence on this point was obtained in the present work.

ACKNOWLEDGEMENTS

The investigation formed part of the programme of research of the Physical Metallurgy Section of the Commonwealth Scientific and Industrial Research Organization, Australia. The work was carried out at the Baillieu Laboratory, University of Melbourne, under the general direction of Professor J. Neill Greenwood, to whom the author expresses his thanks.

Mr. J. A. Corbett performed all the chemical analyses, and the United States Bureau of Mines kindly supplied the commercial titanium.

REFERENCES

1. W. L. Finlay, R. I. Jaffee, R. W. Parcel, and R. C. Durstein, *J. Metals*, 1954, **6**, 25.
2. F. A. Crossley and H. D. Kessler, *Trans. Amer. Inst. Min. Met. Eng.*, 1954, **200**, 119.
3. M. Manjoine, *Trans. Amer. Soc. Mech. Eng.*, 1945, **67**, 111.
4. F. D. Rosi and F. C. Perkins, *Trans. Amer. Soc. Metals*, 1953, **45**, 972.
5. J. N. Pratt, W. J. Bratina, and B. Chalmers, *Acta Met.*, 1954, **2**, 203.
6. M. K. McQuillan, *J. Inst. Metals*, 1953-54, **82**, (9), 433.

MICROSTRUCTURES OF ALUMINIUM ALLOYS OF HIGH YOUNG'S MODULUS.

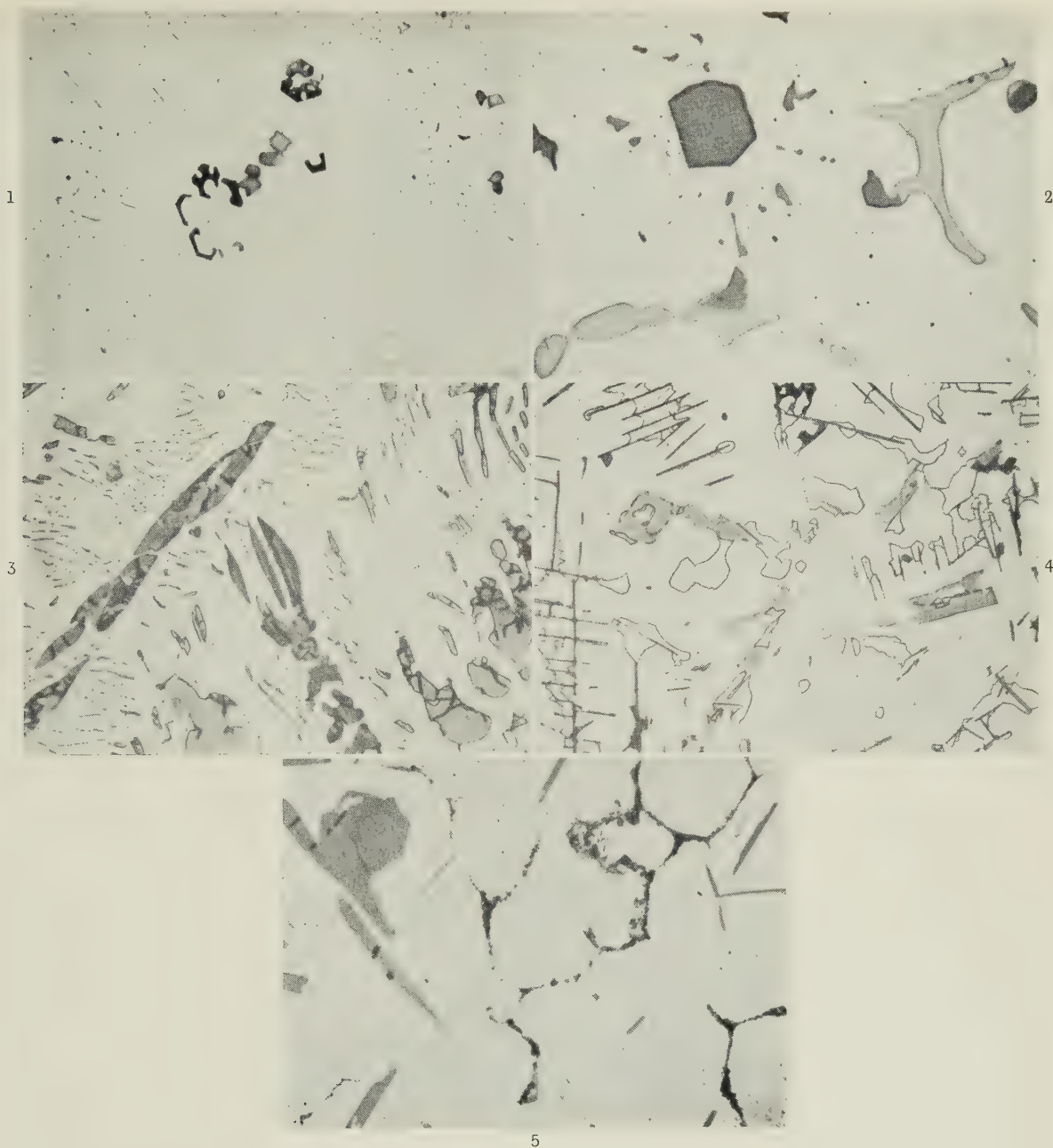


FIG. 1.—Alloy Containing Cobalt 0.80, Beryllium 2.25%. Al + Be (dark) + Co_2Al_9 (half tone) + Al-Be eutectic. Polished electrolytically, unetched. $\times 500$.

FIG. 2.—Alloy Containing Copper 8.32, Beryllium 1.35%. α + CuAl_2 + Be (dark) + Al-Cu-Be (half tone) + Al-Be eutectic. Unetched. $\times 1000$.

FIG. 3.—Alloy Containing Nickel 3.23, Iron 2.93%. NiAl_3 (dark) + FeNiAl_9 (half tone) + ternary eutectic. Etched in 5% KOH, followed by a solution of 0.5% HF, 1.5% HCl, and 2.5% HNO_3 . $\times 500$.

FIG. 4.—Alloy Containing Manganese 4, Magnesium 12.84%. α + Mg_2Al_3 (outlined light) + MnAl_6 (half tone) + $T(\text{MnMg})$ (dark needles). Etched in 0.5% HF. $\times 500$.

FIG. 5.—Alloy Containing Titanium 1.02, Combined Nitrogen 0.10%. Al + TiAl_3 (half tone) + TiN (dark). Unetched. $\times 500$.

PHOTOMICROGRAPHS OF ALUMINIUM-3.5% COPPER ALLOY SINGLE CRYSTALS.

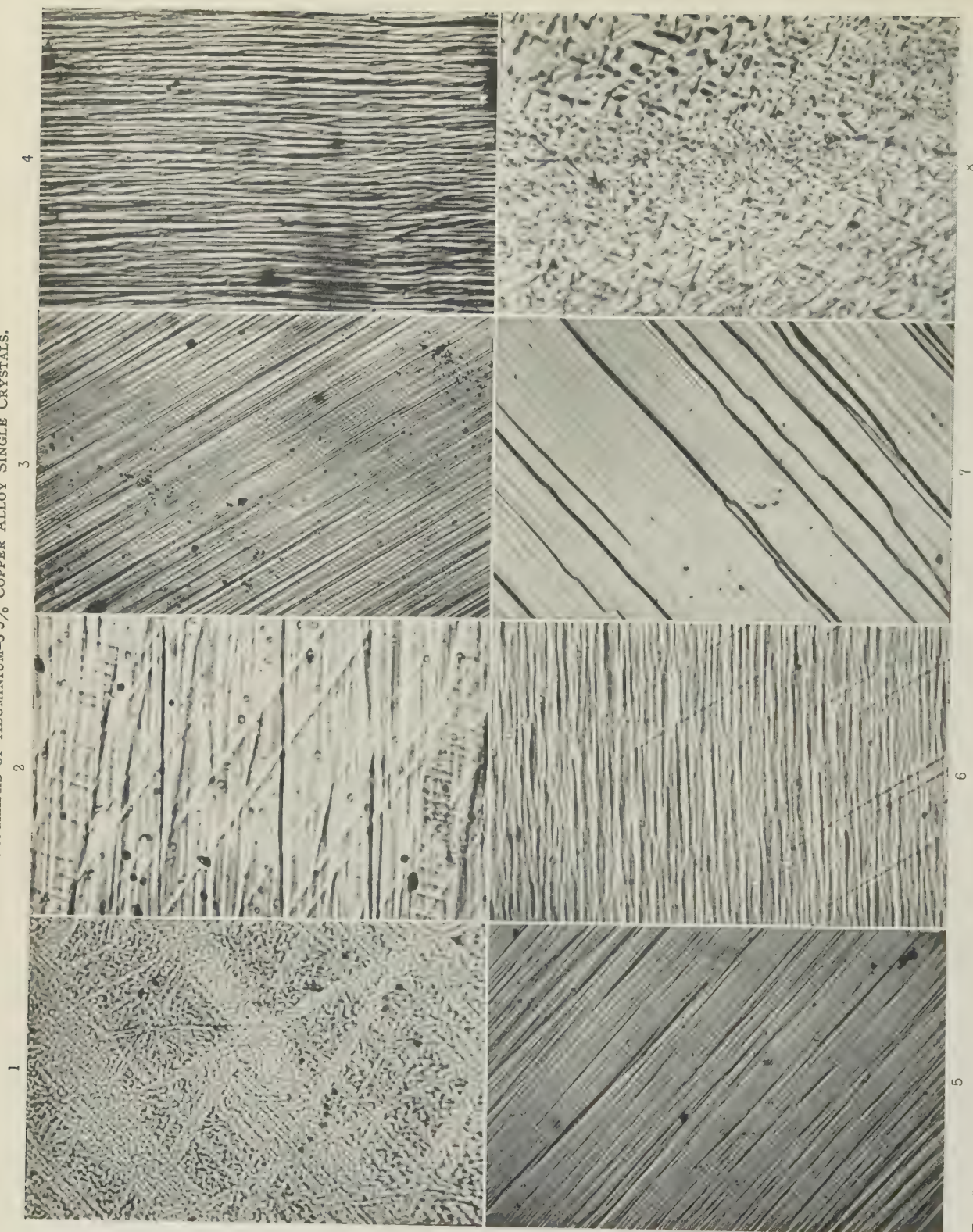


FIG. 1.—Water-Quenched from 535° C.; Subsequently Aged at 300° C. for 30 min. $\times 200$.

FIG. 2.—Water-Quenched from 535° C.; Polished, then Deformed to 10% Extension. $\times 370$.

FIG. 3.—One Face of Crystal 15, Air-Cooled, then Deformed to 17% Extension. $\times 200$.

FIG. 4.—An Adjacent Face of Crystal 15 after 17% Extension. $\times 200$.

FIG. 5.—Crystal 3, Air-Cooled, then Deformed to 50% Extension. $\times 200$.

FIG. 6.—Crystal 15 after 33% Extension. $\times 200$.

FIG. 7.—Crystal 12, Air-Cooled, then Deformed to Fracture. Necked region. $\times 700$.

FIG. 8.—Crystal 12, Air-Cooled, then Deformed to 130% Extension. $\times 700$.

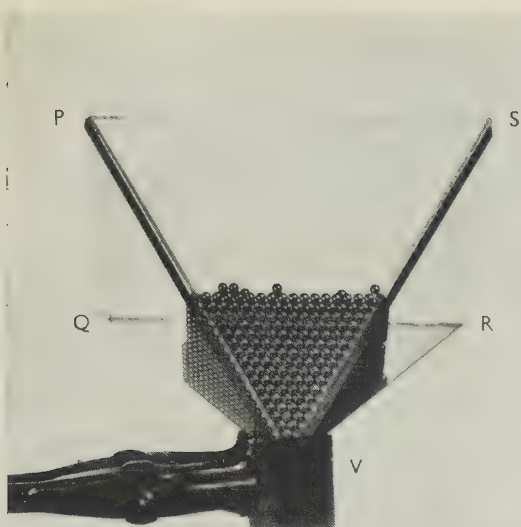


FIG. 3.—General View of Pyramidal Model Taken from About the Point *H* in Fig. 1.

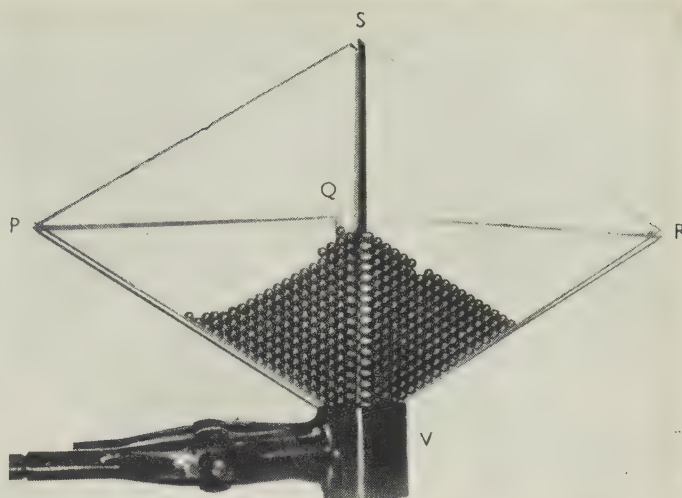


FIG. 4.—Side View of Model After Twinning.

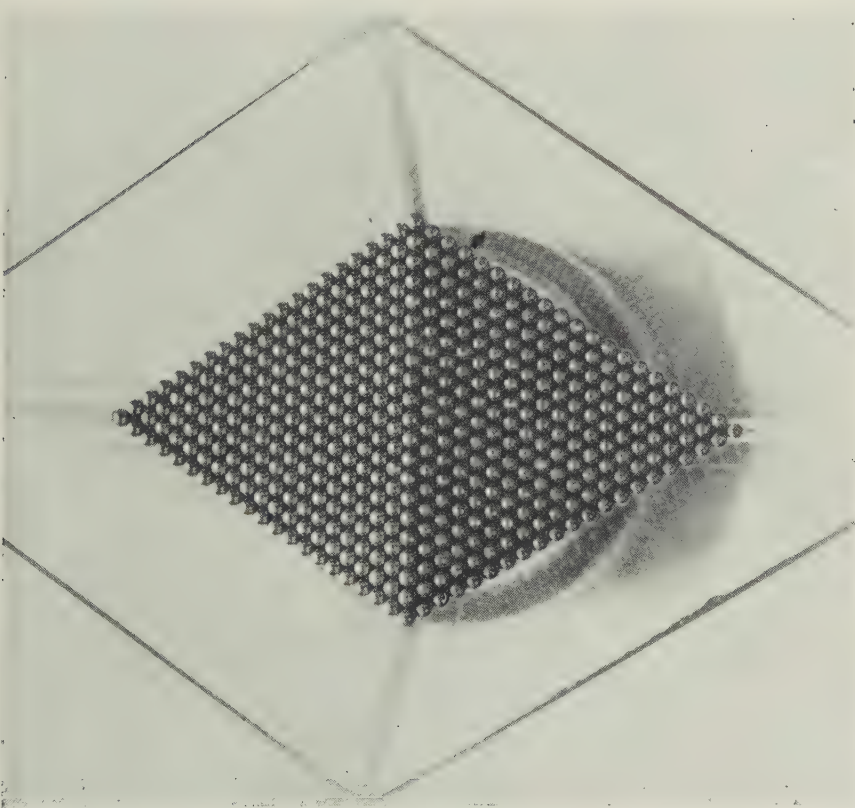


FIG. 5.—Top View of Model After Twinning.

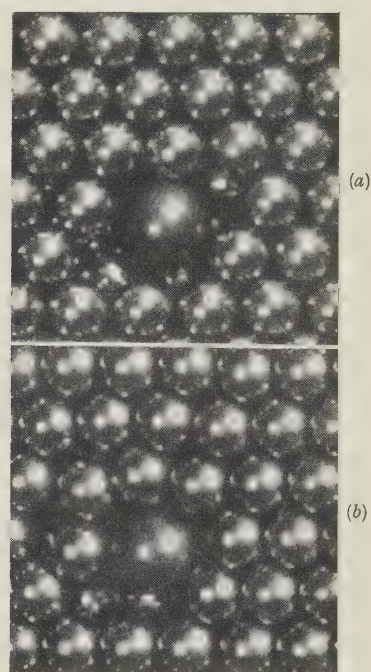


FIG. 6.—Illustrating Distortion of Lattice Arising from Introduction of Larger "Solute" Sphere. (a) Sphere and attendant holes occupying exact number of lattice sites (no distortion). (b) Misalignment following compression of model along a diagonal.

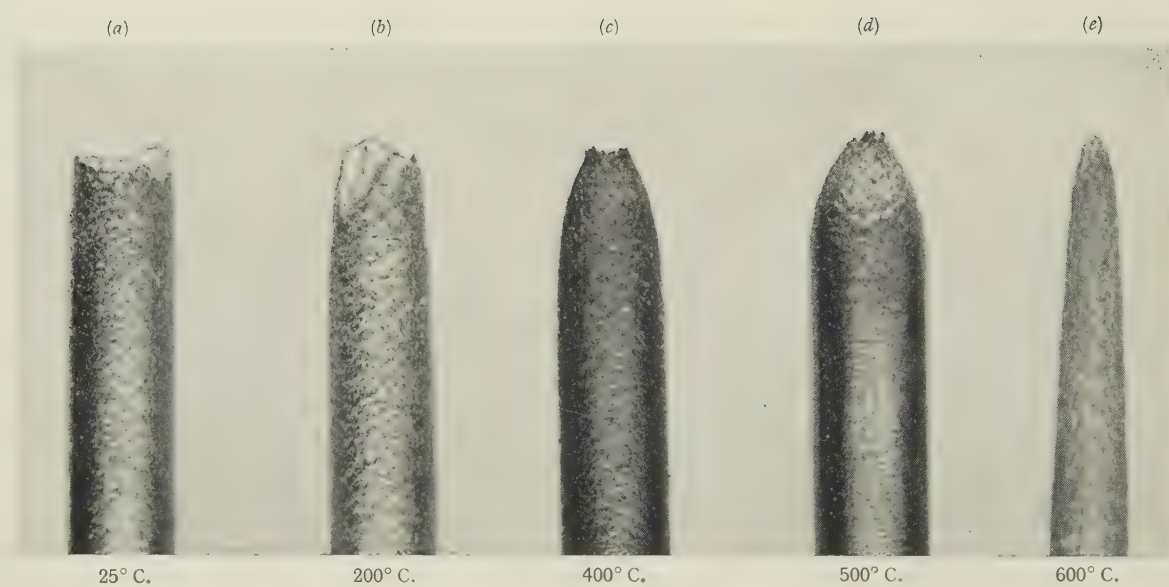


FIG. 8.—Specimens of the Titanium-0.9 At.% Nitrogen Alloy Fractured at the Temperatures Shown.

CREEP BEHAVIOUR AT 300° C. OF A GROUP OF PRECIPITATION-HARDENING ALLOYS BASED ON THE ALPHA COPPER-ALUMINIUM PHASE*

1622

By J. P. DENNISON,† B.Sc., Ph.D., JUNIOR MEMBER

SYNOPSIS

The creep, creep-rupture, and hot-tensile characteristics of six precipitation-hardening alloys based on the α copper-aluminium phase have been examined at 300° C. Specimens tested in the solution-treated, slowly cooled, and aged states have been subjected to detailed metallographic examination.

Alloys containing cobalt, iron, and nickel, which exhibited a form of discontinuous precipitation at the grain boundaries at normal ageing temperatures, showed strain-induced boundary precipitation during test. In these cases a reduction in creep ductility ensued, which was generally associated with internal cracking. For such alloys the slowly cooled state gave the best combination of properties.

Alloys containing titanium or zirconium showed a high ductility at all strain rates.

The principal effects of precipitation before test were to reduce the period and extent of transient creep and to favour the development of fracture.

I.—INTRODUCTION

A PREVIOUS paper¹ has dealt with some observations on the creep performance of selected precipitation-hardening alloys based on the α copper-aluminium phase. All those tests were carried out at 450° C., a temperature at which precipitation proceeded at an appreciable rate during reheating. The present paper is concerned with the creep behaviour of some of these alloys at 300° C., a temperature at which neither hardness change nor visible precipitation occurred during reheating for periods up to 1000 hr.

The object of the present work was to provide creep data on precipitation-hardening alloys, in various initial states and over a wide range of applied stresses, at a temperature where any structural changes in the unstressed condition take place at extremely slow rates, if at all. A detailed metallographic examination has been made of the effect of structure on the

The alloys selected for these tests, listed in Table I, were prepared from 99.98% aluminium and M.C.3-grade, fire-refined copper, of the following analysis: copper 99.93, nickel 0.005, bismuth 0.0003, and oxygen 0.05%.

II.—EXPERIMENTAL PROCEDURE

1. FABRICATION OF ALLOYS

The methods used for the preparation of the alloys in the form of strip have been described in detail in the previous paper, where their precipitation-hardening behaviour has also been recorded. One further alloy, that containing 0.73% titanium, was prepared for the present work.

The four states chosen for testing were: (a) solution-treated, (b) solution-treated and aged to maximum hardness, (c) solution-treated and overaged by ageing to peak hardness at 600° C., and (d) slowly cooled from the solution-treatment temperature. A summary of the treatments involved is given in Table II.

The final specimen sizes before shaping were $4 \times 1 \times \frac{1}{16}$ in. for creep-rupture and hot-tensile tests, and $4 \times 1 \times \frac{1}{16}$ in. for the creep tests.

A solution-treatment temperature of 1000° C. was adopted for the alloys containing cobalt, iron, and nickel, and a temperature of 950° C. for the 0.60% zirconium alloy and the 0.73% titanium alloy. Solution-treatment was carried out in air in view of the high oxidation-resistance of all the alloys.

Differences in grain-size between the various alloys were unavoidable, but very little variation occurred

TABLE I.—Composition of Alloys.

Nominal Composition		Actual Composition		
Al, %	Alloying Element, %	Cu, %	Al, %	Alloying Element, %
7	1.5 Co	91.58	6.85	1.54
7	1.0 Co, 1.0 Fe	91.23	6.71	1.09 Co, 0.96 Fe
7	1.6 Co, 5 Ni	86.41	6.88	1.72 Co, 4.97 Ni
6	1.5 Fe	92.30	6.16	1.52 Fe
6	0.75 Ti	92.95	6.23	0.73 Ti
7	0.6 Zr	92.51	6.86	0.60 Zr

hot-tensile, creep-rupture, and creep properties, in an attempt to account for the experimental results reported.

* Manuscript received 22 September 1954; in revised form 14 February 1955.

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in specimens of the same alloy. Actual grain-size ranges are included in Table II.

Ageing to maximum hardness attainable and ageing to peak hardness at 600° C. were carried out in accordance with the data previously reported.¹ These treatments are summarized in Table II. In each case ageing followed the standard solution-treatment. After ageing, the specimens were allowed to cool in air.

The specimens that were to be slowly cooled were first given the normal solution-treatment in a horizontal furnace. The temperature was subsequently lowered at approximately 5° C./hr. for 40 hr. and then at 2° C./hr. for 150 hr., after which the alloys were soaked at 500° C. for a further 60 hr. The resulting

material, together with a sample in the initial state and one of a strip of material from the unstressed part of the specimen head, which had been exposed at the test temperature. Note was taken of the appearance and distribution of external cracks. This procedure was adopted in all tests where fracture occurred.

(b) Creep-Rupture Tests at 300° C.

The preparation of the specimens and the method of testing were essentially the same as those described for the tests carried out at 450° C.¹ The aim of the present series of creep-rupture tests was to vary the applied stress in order to give results relating time to fracture with applied stress, as indicated in Figs. 1-3.

TABLE II.—Summary of Treatments of Alloys.

Alloy Composition, %	Solution-Treatment			Slow Cooling			Ageing to Max. Hardness after Solution-Treatment			Ageing to Peak Hardness at 600° C. after Solution- Treatment			Average Grain- Size Range, grains/ mm.
	Temp., °C.	Time, hr.	D.P.N.	Temp. Range, °C.	Time, hr.	D.P.N.	Temp., °C.	Time, hr.	D.P.N.	Temp., °C.	Time, hr.	D.P.N.	
1.54 Co, 6.85 Al .	1000	1	68	1000-500	250	83	400	40	260	600	2	160	4-5
1.09 Co, 0.96 Fe, 6.71 Al .	1000	1	70	1000-500	250	72	500	50	175	600	8	150	4-5
1.72 Co, 4.97 Ni, 6.88 Al .	1000	1	95	1000-500	250	135	400	120	370	600	1	235	4-6
1.52 Fe, 6.16 Al .	1000	1	65	1000-500	250	63	500	120*	98	600	10	95	4-5
0.73 Ti, 6.23 Al .	950	2	95	950-500	220	90	400	200	155	600	1	145	12-15
0.60 Zr, 6.86 Al .	950	2	85	950-500	220	79	500	16	107	600	1*	88	12-15

* Nominal treatment.

material was much less subject to structural change on further reheating than it was in the solution-treated or fully aged states in either the stressed or unstressed condition, precipitation of the second phase being much more complete.

2. TESTING PROCEDURE

(a) Hot Tensile Tests at 300° C.

Strip specimens $\frac{1}{16}$ in. thick and 4 in. long, having a gauge-length of 2 in. and a width of $\frac{1}{4}$ in. were assembled in the shackles used for creep-rupture testing and inserted through the 1-in.-dia. stainless-steel tube of a cylindrical furnace 6 in. in dia. and 12 in. long. The latter was fixed in position between opposing jaws of an Amsler 5-ton universal testing machine. The specimen was held at test temperature for sufficient time to establish a constant temperature along its length, this being determined by experiment to be approximately 15 min.

Automatic loading was then begun, and a constant rate of extension of 22% per min. was maintained until fracture occurred. The ultimate tensile strength and total elongation were recorded for a marked gauge-length of 2 in. In view of the errors introduced in fitting fractures, the latter figure is reported to the nearest 0.5% of elongation.

A section of each specimen at fracture was mounted in thermo-setting Bakelite for metallographic examin-

(c) Creep Tests at 300° C.

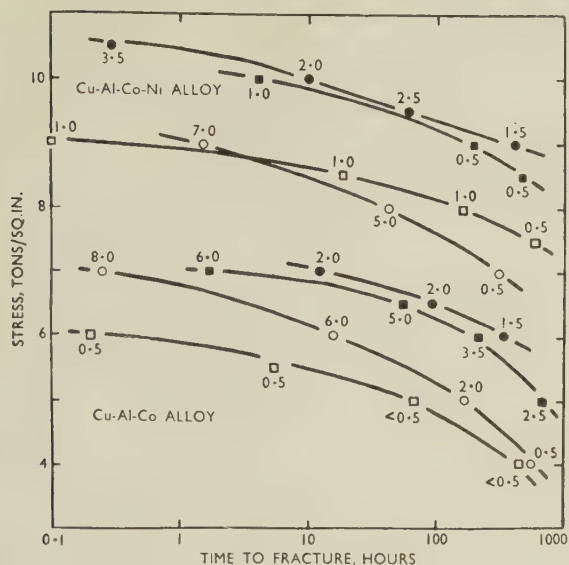
The creep tests reported in Table IV were carried out in Denison T.47-type creep machines modified to take strip specimens of 4 in. overall length, $2 \times \frac{1}{4}$ in. gauge-length, and $\frac{1}{16}$ in. thick. These were prepared as for hot-tensile and creep-rupture tests.

Temperature control was obtained to within $\pm 1^\circ$ C., with a variation of not more than 2° C. along the gauge-length. The extensometers used were capable of being read directly to 0.0001 in., and an estimate to 0.00001 in. was possible. Operating through a 2:1 lever arm, the latter represented a change of 0.00025% in the specimen. The lowest rate of strain recorded was approximately $10^{-4}\%$ per hr. A common initial stress of 4 tons/in.² was employed, which was sufficiently low to preclude the onset of tertiary creep or fracture during the 300-hr. test period.

III.—EXPERIMENTAL RESULTS

Table V summarizes the results of detailed visual and metallographic examination of the specimens whose performances in hot-tensile, creep-rupture, and creep tests at 300° C. are recorded in Figs. 1-3 and Tables III and IV.

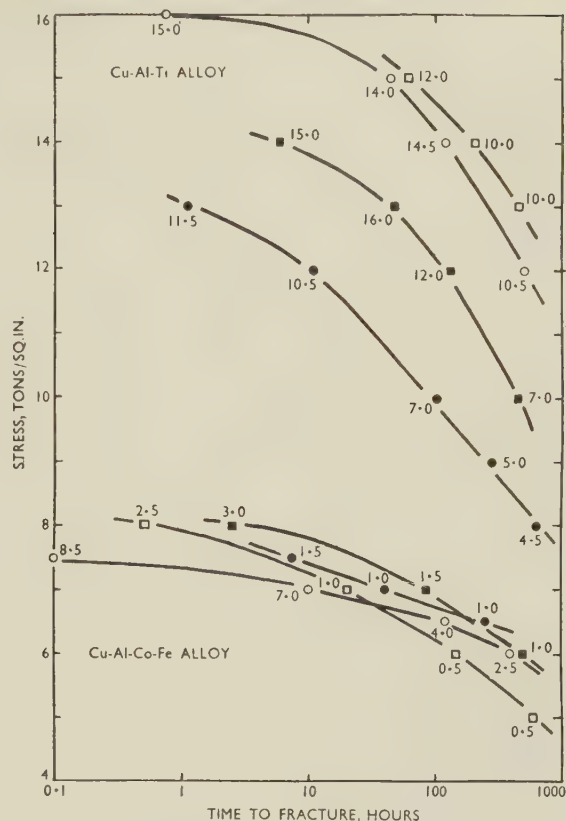
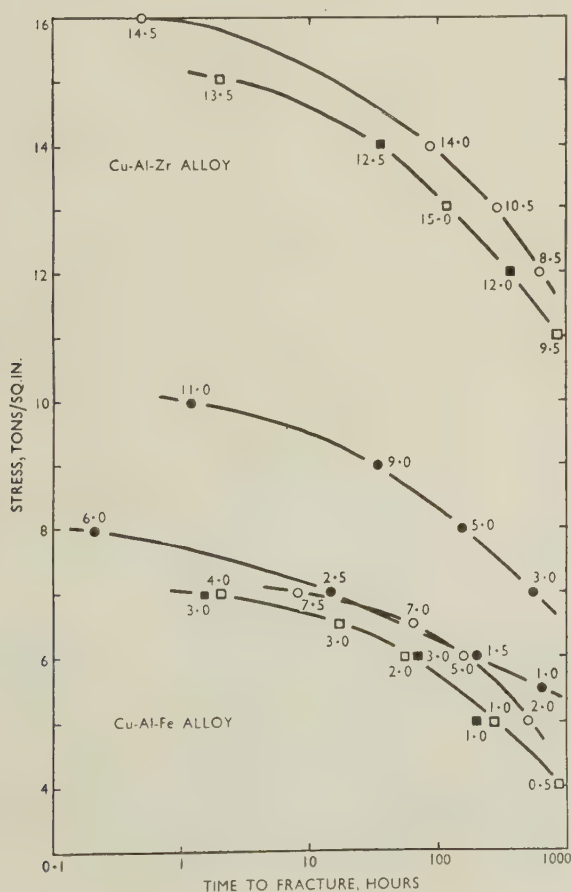
A general feature of tests that were continued to rupture was the occurrence of mixed fractures during a period of transition from entirely transgranular to



FIGS. 1-3.—Stress/Time Curves for α -Copper-Aluminium-Phase Alloys.

KEY.

- Solution-treated.
 - Slowly cooled.
 - Aged to peak hardness at 600° C.
 - Aged to max. hardness.
- Total elongation (%) at fracture is shown beside each point.



entirely intergranular cracking. Edge-cracking occurred in all cases where intergranular failure resulted, the number of such cracks increasing with

TABLE III.—Results of Hot-Tensile Tests at 300° C.

Alloy Com- position, %	Solution-treated		Slowly Cooled		Aged to Max. Hard- ness		Aged to Peak Hardness at 600° C.	
	U.T.S., tons/ in. ²	Elong., %	U.T.S., tons/ in. ²	Elong., %	U.T.S., tons/ in. ²	Elong., %	U.T.S., tons/ in. ²	Elong., %
1.54 Co, 6.85 Al.	10.6	18.0	10.3	7.5	19.2	0.5	15.4	4.5
1.09 Co, 0.96 Fe, 6.71 Al.	13.0	20.0	15.8	15.0	18.5	3.0	15.5	6.0
1.72 Co, 4.97 Ni, 6.88 Al.	21.0	33.0	13.5	5.0	33.8	0.5	30.7	0.5
1.52 Fe, 6.16 Al.	12.4	22.0	12.4	14.0	11.8	8.0	12.0	12.0
0.73 Ti, 6.23 Al.	25.0	27.0	19.2	16.0	23.5	17.0	23.5	15.0
0.60 Zr, 6.86 Al.	24.0	38.0	15.5	19.0	20.6	24.0	18.6	23.0

creep-rupture life. As noted in Table V, internal cracking was also evident in solution-treated and in fully hardened specimens containing cobalt, iron, and nickel. In these specimens internal cracking at low strain rates was accompanied by the formation of cavities along boundaries having appreciable inclination to the direction of applied stress.

Although strain-induced precipitation took place in grain-boundary regions in solution-treated specimens, no significant degree of hardening occurred, and on etching general staining, pronounced in the pre-aged alloys, was absent.

TABLE IV.—Results of Creep Tests at 300° C. under Stress of 4 tons/in.².

Alloy Composition, %	Condition	Approx. Total Extension in Primary Stage, %	Approx. Duration of Primary Stage, hr.	2nd Stage Steady Rate After 300 hr., % per hr. $\times 10^{-4}$	Total Extension After 300 hr., %
1.54 Co, 6.85 Al	S.T.	0.15	100	1.5	0.20
	S.C.	0.22	40	8.0	0.43
	A.M.H.	0.13	25	3.0	0.22
	A. 600° C.	0.14	30	5.0	0.28
1.09 Co, 0.96 Fe, 6.71 Al	S.T.	0.26	130	0.8	0.28
	S.C.	0.30	80	2.7	0.36
	A.M.H.	0.20	80	1.0	0.22
	A. 600° C.	0.22	60	3.0	0.30
1.72 Co, 4.97 Ni, 6.88 Al	S.T.	0.20	100	0.7	0.22
	S.C.	0.22	50	1.3	0.24
	A.M.H.	0.12	80	0.9	0.14
	A. 600° C.	0.18	50	1.5	0.23
1.52 Fe, 6.16 Al	S.T.	0.50	170	5.5	0.57
	S.C.	0.30	50	8.5	0.53
	A.M.H.	0.22	40	4.0	0.30
	A. 600° C.	0.19	40	5.0	0.36
0.73 Ti, 6.23 Al	S.T.	0.17	60	2.5	0.21
	S.C.	0.35	60	10.0	0.60
	A.M.H.	0.15	40	2.5	0.19
	A. 600° C.	0.16	40	4.0	0.25
0.60 Zr, 6.86 Al	S.T.	0.18	40	2.0	0.22
	S.C.	0.31	40	4.5	0.42
	A.M.H.	0.13	40	2.0	0.18
	A. 600° C.

S.T. = Solution-treated. S.C. = Slowly cooled. A.M.H. = Aged to maximum hardness. A. 600° C. = Aged to peak hardness at 600° C.

IV.—DISCUSSION OF RESULTS

The creep-rupture results illustrated in Figs. 1-3 show that for any of the alloys in the slowly cooled condition an approximately linear relationship exists between applied stress and log time for times to fracture of the order of 10 hr. or more. A similar relationship appears to hold for the alloys containing titanium or zirconium in all other conditions after a somewhat longer initial period has elapsed. This period approximately coincides with the time of change-over from transgranular to intergranular fracture. The remaining alloys tested in the solution-treated and aged states show considerable divergence from such a relationship, the tendency being for an earlier development of fracture at low strain rates.

It has been observed, in both the present work and in that reported earlier for higher temperatures,¹ that in the alloys susceptible to a form of discontinuous precipitation in grain-boundary regions, internal intergranular cracking occurred, often during the period for which a linear extension/time relationship held. In the earlier paper it was suggested that an impoverishment in solute atoms near the boundaries, due to precipitation, might permit a relaxation of stress along the boundaries having initial inclina-

tions approximately parallel to the direction of applied stress. This would lead to a concentration of stress on boundaries almost perpendicular to the direction of stress. Bodily movement of the latter by grain elongation would be restricted by the presence of the precipitate and cracking would start. It was noted that similar phenomena had been observed by earlier workers, notably Perryman and Blade,² in their work on stress-corrosion of aluminium-zinc alloys.

A similar method of accounting for intergranular embrittlement, particularly at high temperatures, has recently been proposed by Eborall.³ He suggested that stress is concentrated along boundaries normal to the applied stress, which are so placed that they cannot relieve the increasing concentration of stress by viscous flow. This stress can thus be relieved either by movement elsewhere, i.e. within the grains, or by fracture at these boundaries. Eborall indicates that yielding of the grains with subsequent stress-relief will take place with soft materials, and that in such a case intercrystalline fracture may occur only after sufficient time has elapsed for the grains to become strain-hardened.

From these observations it appears that grain-boundary precipitation may increase the susceptibility of a given alloy to intercrystalline fracture. A considerable reduction in ductility should result if either precipitation or a pre-precipitation process sufficient to prevent slip has also occurred within the lattice and thus inhibited relief of stress in the boundaries concerned.

The experimental results described for the alloys containing cobalt, iron, and nickel, are in accordance with these views. In all cases, the specimens pre-aged to maximum hardness showed the lowest ductility in tests continued to fracture.

In the overaged condition, precipitation was generally continuous. The specimens were more stable at test temperature and not so subject to localized impoverishment in solute atoms; this possibly accounted for their improved creep-rupture performance. Sully and Hardy⁴ have also recently noted a weakening of metal adjacent to grain boundaries by depletion of solute atoms due to grain-boundary precipitation.

The overall creep rates shown by alloys in the pre-aged and overaged conditions were not markedly different. In the former case, however, the lattice would have offered greater resistance to movement and hence a lower ductility and generally more rapid fracture would be expected to result.

The behaviour of solution-treated alloys in this series was more complex. At high strain rates, appreciable elongations were obtained, although in the case of the alloys most subject to rapid precipitation, as indicated in Table V, intergranular fractures resulted. The structural instability of these alloys while under stress is reflected in the increased periods of transient creep (Table IV). In the case of the copper-aluminium-iron specimen, in which precipitation was

TABLE V.—Structure and Fracture of Specimens.

Alloy	Condition	Initial Structure	Type of Fracture and Associated Cracks		Metallographic Change During Hot Tensile, Creep-Rupture or Creep Tests
			Hot Tensile	Creep Rupture (lives greater than 5 hr.)	
1.54 Co, 6.85 Al	S.T.	Single phase.	Intergranular. Edge-cracking.	Intergranular. Internal cracking.	Solution-treated alloy showed boundary precipitation at all strain rates. Internal cracks formed at tri-boundaries at high strain rates and along favourably inclined boundaries at low strain rates (Fig. 7, Plate LXX).
	S.C.	Uniform distribution of 2nd phase. Narrow size range approx. that of larger particles in Fig. 4 (Plate LXX).	Transgranular. Necking.	Intergranular.	
	A.M.H.	Precipitation at grain boundaries. Lattice staining on etching.	Intergranular. Single crack.	Intergranular. Internal cracking.	
	A. 600° C.	Continuous precipitation throughout structure.	Transgranular.	Intergranular.	
1.09 Co, 0.96 Fe, 6.71 Al	S.T.	Single phase.	Transgranular.	Intergranular. Internal cracking at low strain rates.	Solution-treated alloy showed boundary precipitation after periods of test greater than 100 hr. Internal cavities formed at intervals along boundaries with high inclination to direction of applied stress.
	S.C.	Uniform distribution of 2nd phase. Wide size range. As Fig. 4, with heavier precipitation.	Intergranular. Necking.	Intergranular.	
	A.M.H.	Precipitation at grain boundaries.	Intergranular. Edge-cracking.	Intergranular. Internal cracking.	
	A. 600° C.	Continuous precipitation throughout structure, Fig. 5 (Plate LXX).	Transgranular.	Intergranular.	
1.72 Co, 4.97 Ni, 6.88 Al	S.T.	Single phase.	Intergranular. Internal and edge-cracking.	Intergranular. Internal cracking.	Solution-treated alloy showed boundary precipitation at all strain rates. Internal cracking as for Cu-Al-Co alloy (see Fig. 7, Plate LXX).
	S.C.	Wide size range of 2nd phase. Large particles enveloping boundaries, Fig. 6 (Plate LXX).	Intergranular. Edge-cracking.	Intergranular.	
	A.M.H.	Precipitation at boundaries. Heavy staining on etching.	Intergranular. Single crack.	Intergranular. Internal cracking.	
	A. 600° C.	Continuous precipitation throughout structure.	Intergranular. Single crack.	Intergranular.	
1.52 Fe, 6.16 Al	S.T.	Single phase.	Transgranular.	Intergranular. Internal cracking at low strain rates.	Solution-treated alloy showed "double" boundaries (migration?) (Fig. 8, Plate LXX). Precipitation apparent on both boundaries after long periods of test. Internal cracking as for Cu-Al-Co-Fe alloy.
	S.C.	See Fig. 4 (Plate LXX).	Transgranular. Necking.	Mixed. Intergranular at low strain rates.	
	A.M.H.	Precipitation at boundaries.	Mixed. Intergranular edge-cracking.	Intergranular. Internal cracking.	
	A. 600° C.	Precipitation at boundaries.	Transgranular.	Intergranular. Internal cracking at low strain rates.	
0.73 Ti, 6.23 Al	S.T.	Single phase. Stringers of oxide inclusions (all states).	Transgranular. Necking.	Intergranular after 100 hr.	Solution-treated alloy showed slight thickening of all grain boundaries. Where elongation was high, some cracks were located in bands parallel to, but slightly inset from, edges.
	S.C.	Random distribution of uniform-size globular precipitate.	Transgranular.	Intergranular.	
	A.M.H.	Continuous precipitation throughout structure. Particles resolved at 200 ×.	Transgranular.	Intergranular after 50 hr.	
	A. 600° C.	Continuous precipitation throughout structure. Particles resolved at 5 ×.	Transgranular.	Intergranular after 50 hr.	
0.60 Zr, 6.86 Al	S.T.	Light random distribution of globular undissolved 2nd phase.	Transgranular. Necking.	Intergranular after 100 hr.	No visible change. Cracking similar to Cu-Al-Ti alloy.
	S.C.	Heavier and coarser random precipitation of 2nd phase.	Transgranular.	Intergranular.	
	A.M.H.	No visible precipitation.	Transgranular.	Intergranular after 50 hr.	
	A. 600° C.	No visible precipitation. Continuous precipitation after considerable over-ageing.	Transgranular.	Intergranular after 50 hr.	

S.T. = Solution-treated. S.C. = Slowly cooled. A.M.H. = Aged to maximum hardness. A. 600° C. = Aged to peak hardness at 600° C.

relatively slow, the occurrence of an unusual boundary phenomenon has been noted (Table V and Fig. 8, Plate LXX). This apparent boundary movement did not occur in pre-aged specimens of the same alloy. A somewhat similar case, the blocking of cyclic processes at grain boundaries by precipitation, has been reported by Roberts in a magnesium-cerium alloy.⁵

The relatively small differences in steady creep rate between solution-treated and pre-aged specimens suggest that the maximum reduction in this rate, for a given alloy, might be obtained by a critical dispersion of the precipitating phase within the lattice. This dispersion might occur at an earlier stage than that necessary to achieve a significant degree of hardening.

Some observations by Glen^{6,7} on low-alloy steels compare the effects of precipitation before and during deformation. Where precipitation occurred during deformation, the pre-aged alloy exhibited a higher rate of secondary-stage creep at high temperatures, whereas at low temperatures the reverse was true. This contrasts to some extent with the present results, which can be regarded as having been obtained at low temperatures in the sense that the unstrained structures were stable.

Coarse precipitation, as observed during slow cooling, resulted in an increased rate of secondary creep, under the stress used in the present tests. The elongations at fracture reported in Figs. 1-3 appear to suggest that for material in the slowly cooled state the effect of increasing stress on total elongation in a given period is less marked than for solution-treated or aged specimens.

The main effect of slow cooling might be to reduce the tendency for precipitation-hardening alloys of this type to become embrittled owing to structural changes taking place during test. Jenkins, Bucknall, and Jenkinson,⁸ in their work on the creep-rupture characteristics of a copper alloy containing nickel and silicon, also concluded that the slowly cooled condition was superior to the pre-aged or solution-treated state at low stresses.

A consideration of the fracture characteristics of the alloys containing cobalt, iron, and nickel, indicates that the development of intergranular cracking may be in accordance with the theories outlined by Greenwood⁹ and by Greenwood, Miller, and Suiter¹⁰ in explaining the cause of intercrystalline cracking of α -brass at elevated temperatures. The occurrence of minute cavities in boundaries approximately normal to the direction of stressing and the linking of these cavities to form a crack have been observed for both solution-treated and pre-aged specimens (Table V and Fig. 7, Plate LXX). Greenwood *et al.*¹⁰ show that cavitation appears more readily under conditions where there is a change in emphasis from deformation by slip to deformation by grain transfer. These conditions normally obtain at high temperatures and low strain rates.

The experiments of McLean and Farmer¹¹ indicate that the slip and grain-boundary displacement in

binary aluminium alloys take place concurrently and bear a constant ratio to one another during a given test. In the present tests it appears that, because of the precipitation characteristics, this ratio of boundary flow to slip may be greater than that in similar alloys in which precipitation does not occur, or in the same material in the slowly cooled state. It is noteworthy that slowly cooled specimens were far less liable to develop cavities of this nature. The mechanism involved in the initial formation of such internal cracks, particularly those starting along sloping boundaries, remains obscure, however.

Somewhat different behaviour is evident in the results reported for alloys containing titanium or zirconium. Ductility was relatively unaffected by initial condition, with the exception of slow cooling, which caused a marked reduction. Eborall³ has recently pointed out that the addition of zirconium to tin bronzes considerably increases hot ductility and also improves the creep life and elongation at fracture. He suggested that this was not a case of inhibition of grain-boundary relaxation, but rather that the fracture process itself was affected. Eborall notes that the improved fracture characteristics are due to small additions of high-melting-point elements of "unfavourable" size-factor. The characteristics of the solid solution, rather than precipitation effects, may thus be largely responsible for the enhanced hot-tensile, creep, and creep-rupture properties of the copper-aluminium-titanium and copper-aluminium-zirconium alloys. A contributing factor may be the smaller grain-size shown by these alloys. General impoverishment of the solid solution resulting from slow cooling led to an all-round decrease in properties.

V.—CONCLUSIONS

(1) In a series of alloys based on the α copper-aluminium phase, two distinct types of behaviour were observed. The alloys containing additions of cobalt, iron, and nickel were susceptible to intergranular fracture which could be ascribed to precipitation effects. The increased ductility of alloys containing titanium or zirconium is believed to be an inherent property of the solid solution.

(2) Inhibition of lattice slip by a precipitation process led to a considerable loss in permissible extension during creep. The latter has been attributed to a build-up of stress in boundaries initially approximately normal to the applied stress, and would occur more rapidly if an impoverished solid solution existed in grain-boundary regions.

(3) Strain-induced ageing took place in grain-boundary regions for all the alloys examined at 300° C., a temperature at which unstrained structures were stable. The rate at which precipitation occurred increased the duration of transient creep in the alloy concerned, and such precipitation was effective in reducing the creep rate.

(4) The emphasis on grain-boundary movement

may have provided the conditions for initiation of boundary cavities and thus accelerated intergranular fracture.

(5) The effects of pre-ageing and overaging were more marked in reducing initial extension and tran-

sient creep, and on the development of fracture, than on steady-state creep.

(6) In alloys subject to embrittlement on precipitation, the slowly cooled structure may provide a more useful combination of creep rate and ductility.

REFERENCES

1. J. P. Dennison, *J. Inst. Metals*, 1953-54, **82**, 117.
2. E. C. W. Perryman and J. C. Blade, *ibid.*, 1950, **77**, 263.
3. R. Eborall, *N.P.L. Symposium on Creep*, 1954, (Paper No. 17).
4. A. H. Sully and H. K. Hardy, *J. Inst. Metals*, 1953-54, **82**, 264.
5. C. S. Roberts, *Trans. Amer. Inst. Min. Met. Eng.*, 1954, **200**, 634.
6. J. Glen, *J. Iron Steel Inst.*, 1948, **158**, 37.
7. J. Glen, *A.S.T.M. Special Tech. Publ.*, 1952, (**128**), 184.
8. C. H. M. Jenkins, E. H. Bucknall, and E. A. Jenkinson, *J. Inst. Metals*, 1944, **70**, 57.
9. J. Neill Greenwood, *Bull. Inst. Metals*, 1952, **1**, 104, 120.
10. J. Neill Greenwood, D. R. Miller, and J. W. Suiter, *Acta Met.*, 1954, **2**, 250.
11. D. McLean and M. H. Farmer, *J. Inst. Metals*, 1954-55, **83**, 1.

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THE EQUILIBRIUM DIAGRAM OF THE SYSTEM NICKEL-TITANIUM *

1623

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SYNOPSIS

The equilibrium diagram of the system nickel-titanium has been investigated above 900° C. by thermal, microscopical, and X-ray methods. The addition of titanium to nickel produces a marked depression of the liquidus and solidus curves, which sink to a eutectic at 1304° C., the solid phases being the solid solution in nickel and the phase Ni_3Ti . The latter is of almost fixed composition and gives rise to a pronounced maximum on the liquidus at 1380° C. The solid solution in nickel remains supersaturated even after long times of annealing at 1000° C., and it is probable that the true equilibrium curve was not obtained. At 1118° C., there is a eutectic of Ni_3Ti and a phase of slightly variable composition based on the equiatomic ratio NiTi , which gives rise to a maximum on the liquidus curve at 1310° C. The liquidus then falls to 984° C., at which temperature the phase NiTi_2 , of almost fixed composition, is formed by a peritectic reaction. At 942° C. there is a eutectic horizontal of NiTi_2 and the solid solution of nickel in β -titanium; above this both solidus and liquidus rise steeply to the melting point of titanium, which is estimated as 1680° C. Some lattice-spacing data are included.

I.—INTRODUCTION

PREVIOUS work on the system nickel-titanium may be considered under two main headings. On the one hand conventional methods have been used to investigate the system from the nickel-rich end, up to a point at which the alloys become too reactive to be dealt with by normal methods. On the other hand, titanium-rich alloys have been prepared by arc-melting techniques, and the equilibrium relations have been studied in the solid state by microscopical and X-ray methods, and by the hydrogen-pressure method of McQuillan;¹ the alloys were again too reactive for the liquid \rightleftharpoons solid equilibrium to be investigated. As a continuation of previous work on nickel alloys, the present authors have determined the complete equilibrium diagram of the system nickel-titanium above 900° C., and the discussion of previous work is restricted to these higher temperatures.

The early work of Wallbaum and his collaborators,² based on alloys prepared from impure titanium, established the following main points:

(a) There is an appreciable solid solution of titanium in nickel, the solubility falling with decreasing temperature. This solubility curve was later determined by Taylor and Floyd,³ who used magnesium-reduced titanium, and obtained higher solubilities than those of Wallbaum; the details of this work are discussed on p. 478.

(b) The nickel-rich solid solution was shown to form a eutectic with a phase Ni_3Ti which gave rise to a maximum on the liquidus curve, and possessed a

hexagonal close-packed superlattice structure, for which the most accurate cell constants, as determined by Taylor and Floyd,³ are: $a = 2.5454$, ($2a = 5.0907$), $c = 8.2900$ kX, $c/a = 3.2569$ ($c/2a = 1.6284$).

(c) On the titanium-rich side, Ni_3Ti forms a eutectic with a phase of slightly variable composition based on the equiatomic ratio NiTi . According to Wallbaum,² this phase was formed by a peritectic reaction between the liquid and a phase of higher titanium content and higher melting point. While the present work was in progress, a paper appeared by Margolin, Ence, and Nielsen,⁴ who determined the liquidus approximately by a quenching method, and claimed that NiTi gave rise to a maximum on the liquidus curve. This has been confirmed by the present work, but the temperature is about 80° C. higher than that given by Margolin, Ence, and Nielsen. According to Laves and Wallbaum,⁵ NiTi has a body-centred cubic structure of the caesium chloride type. Its lattice spacing was determined as $a = 2.980$ kX by Duwez and Taylor,⁶ who considered that at 800° or 650° C. the compound decomposes into a mixture of Ni_3Ti and NiTi_2 . Taylor and Floyd give 3.005 kX at 20° C.

(d) The phase NiTi_2 was discovered by Wallbaum,² and was confirmed by later workers. It is formed by a peritectic reaction between liquid and NiTi , and has a face-centred cubic structure with $a = 11.310$ kX (Duwez and Taylor⁶), and 96 atoms per unit cell (Laves and Wallbaum⁵). Rostoker⁷ obtained $a = 11.29$ kX, and described the structure as being of the $\text{Fe}_3\text{W}_3\text{C}$ type, both in the pure state and in the presence of oxygen.

(e) The NiTi_2 phase forms a eutectic with the solid

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§ The double cell constant is for comparison with that of Laves and Wallbaum.⁵

solution of nickel in β -titanium, and there is fair agreement with the results of different workers ^{4, 8} for the β -Ti/(β -Ti + NiTi₂) solid-solubility curve above 900° C., although the solubility relations at lower temperatures are in dispute.

II.—EXPERIMENTAL METHODS

1. MATERIALS USED

The nickel used in the present work was specially selected Mond nickel shot, whose purity was of the order of 99.95%. The metal was presented by The Mond Nickel Co., Ltd., and we thank Mr. H. W. G. Hignett for his help in this connection. The titanium metal was iodide titanium, some of which was supplied by the Pure Metals Committee of the Department of Scientific and Industrial Research, and some was obtained from Imperial Chemical Industries, Ltd. The purity varied between 99.7 and 99.8%, the principal contaminant being iron. For some of the final work on titanium-rich alloys, use was made of a bar of American iodide titanium, of purity 99.9%.

2. LIQUIDUS DETERMINATION

The difficulty of making an accurate determination of the liquidus curve is largely one of avoiding contamination. In all cases it was found best to prepare the alloys first, and then to remelt them in the cooling-curve apparatus described below. For alloys containing up to 40 at.-% titanium,* the initial preparation was carried out by melting the two metals in thoria crucibles in a vacuum H.F. induction furnace. With higher percentages of titanium, the heat of reaction was so great that contamination of the melt occurred owing to attack of the crucible, and the alloys were therefore prepared in an arc-melting furnace. The first of these alloys were prepared at the Atomic Energy Research Establishment, Harwell, and we must express our thanks to Dr. H. M. Finnieston and his colleagues for their great help in this connection. The later alloys were prepared in a small arc-melting furnace designed by one of us (D. M. P.) and built in our laboratory.

For alloys containing more than 78 at.-% titanium, the liquidus was determined by the microscopical method described by Hume-Rothery and Poole.⁹ For alloys of lower titanium content, successful thermal analyses were carried out in the apparatus of Harris and Hume-Rothery,¹⁰ whose paper gives full details of the experimental methods. Melts of 30–100 g. were used, according to the density, and the standard technique of the laboratory¹¹ was followed. The rates of cooling at the freezing points were of the order of 2°–3° C./min., and the experiments were

carried out *in vacuo*. Both thoria and alumina refractories were used for alloys containing less than 50 at.-% titanium, and pure alumina refractories for the range 50–78 at.-% titanium. For the determination of the solidus curve of the nickel-rich solid solution by thermal analyses, the alloy was annealed for about 30 min. at a temperature 10°–15° C. below the expected solidus point, and the heating curve was then taken.

Most of the cooling-curve ingots were sectioned and examined microscopically, and one or both halves were then dissolved for analysis. In all cases both nickel and titanium were determined; the aluminium content † of the alloy was also determined, and many ingots were examined for thorium. Once the danger of overheating from the exothermic reaction or during thermal analysis had been appreciated, the contamination from the refractories was slight, as may be seen from Table I.

TABLE I.—Contamination of Specimens Used for Liquidus Determination.

Composition, Ti at.-%	Max. % Aluminium	Max. % Thorium
0–25 *	0.11	Nil
25–40 *	Trace	"
40–75 †	0.09	...

* Initially prepared by induction melting of nickel and titanium in a thoria or thoria-lined alumina crucible.

† Initially prepared by arc-melting.

3. SOLIDUS DETERMINATIONS

As described above, the solidus curve of the nickel-rich solid solution was determined from arrests on heating curves. The eutectic and peritectic temperatures were determined from arrests on cooling curves, and were confirmed by conventional methods of annealing, quenching, and microscopical examination. For this purpose the alloys were placed in alumina collars inside sealed silica tubes containing dried argon which was admitted in an amount such that the pressure was approximately 1 atm. at the annealing temperature. The annealing was carried out in controlled tubular resistance furnaces, and on quenching the tube was broken with an iron pestle. The same method was used for determining the solidus curve of the NiTi phase, and for the low-temperature portion of the β -titanium solidus.

For alloys of very high titanium contents, the specimen was held in a frame of molybdenum sheet, the arrangement being such that contact with the container occurred at only three or four points formed by centre-punching the sheet before it was bent to shape. After heating for 30 min. at the desired temperature, the specimen was then dropped into

* All compositions in the present paper are in atomic percentages of titanium, and for abbreviation an expression such as alloy 32.5 is used to describe an alloy containing 32.5 at.-% titanium.

† This term is used to describe the aluminium contained in the metallic alloy. Accidental inclusions of alumina from the refractories were weighed separately.

silicone oil, both operations being carried out in a vacuum of about 0.01μ . The furnace for this work was similar to that of Harris and Hume-Rothery,¹⁰ except that the specimen holder was hung by tungsten-molybdenum wire from an iron slug controlled magnetically inside a glass extension to the evacuated furnace tube. The bottom of the furnace was modified to hold a brass can containing silicone oil.

4. DETERMINATION OF PHASE BOUNDARIES IN THE SOLID STATE

The annealing treatments were carried out in platinum-wound resistance furnaces, using standard methods of control.¹¹ All specimens were contained in alumina collars inside sealed, evacuated silica tubes containing argon. After quenching, the alloys were sectioned and examined microscopically. For alloys containing 0–25 at.-% titanium, the most satisfactory etching reagent was found to be a 50% aqueous solution of nitric acid. For alloys of higher titanium content, the best general reagent was a mixture of 6 parts 40% hydrofluoric acid and 3 parts nitric acid in 100 parts (by volume) of water. This reagent does not, however, distinguish clearly between NiTi and NiTi₂, and for this purpose the following special reagent was found to stain NiTi₂ purple, whilst leaving NiTi unattacked: 30 g. manganese chloride, 100 c.c. 2*N* aqueous hydrochloric acid, and 20 c.c. of 3% hydrofluoric acid + 3% nitric acid in water. This reagent was particularly useful for alloys in the range 50–67 at.-% titanium. For titanium-rich alloys some use was made of a chemical “polish-etch” reagent, consisting of 90 c.c. of 100-vol. hydrogen peroxide solution and 10–15 c.c. 40% hydrofluoric acid, which produces a satisfactory surface after grinding to 600 silicon carbide; the solution is based on that described by Cain.¹³

Points on the solubility curve of the nickel-rich solid solution were also determined by X-ray methods. For this purpose lumps of alloy were annealed at, and quenched from, the temperature concerned, and filings were then prepared and annealed at the same temperature in alumina containers inside sealed silica tubes filled with argon. For the lattice-spacing determinations, standard X-ray techniques and extrapolation methods were used.

The crystal structures of the three intermediate phases were confirmed by X-ray powder photographs taken with filtered copper radiation, and accurate parameter values were obtained by standard extrapolation methods.

5. TEMPERATURE MEASUREMENT

All temperature measurements were carried out with platinum/platinum–13% rhodium thermocouples. These were first calibrated against standard freezing points, and a deviation curve drawn for use with

standard tables. Subsequent slight changes were allowed for by frequent calibration against the freezing point of pure nickel.

6. CHEMICAL ANALYSIS

The chemical analyses were carried out by Messrs. Johnson, Matthey and Co., Ltd., and the authors must express their thanks to Mr. A. R. Powell, F.R.S., and to Dr. J. C. Chaston for their care and attention. Cooling-curve ingots were analysed for both metals, and in the earlier work when the suitability of refractories was being examined, determinations were also made of aluminium and/or thorium in the alloy, whilst the iron content was determined in some cases. The analytical totals suggested that any contamination by other elements was very slight. One of the arc-melted and annealed alloys which was thought to have been contaminated was analysed by vacuum-fusion methods, and was found to contain 0.004% oxygen, 0.0015% nitrogen, and 0.0017% hydrogen. For the determination of the boundaries of the phase fields, the critical alloys were analysed for both metals. In all, 83 alloys were analysed, and if the insoluble matter,* iron, and aluminium (appreciable only in the case of two cooling-curve ingots near the equiatomic composition) are included, the analytical percentage totals for 70 specimens lay between 99.95 and 100.05, and for 11 specimens the totals were between 99.90 and 99.95. In the remaining two alloys the totals were between 99.8 and 99.9. The iron contents of the alloys were usually of the order of 0.01–0.04%, the highest value being 0.10% for three of the nickel-rich alloys. Aluminium contents were generally well below 0.05%, but somewhat higher values were found for some cooling-curve ingots (see p. 474).

The method of analysis was as follows: Cooling-curve ingots were dissolved in hydrochloric acid and the solution treated with a minimum of nitric acid to convert the TiCl₃ into TiCl₄. The solution was diluted to a standard volume and appropriate aliquots taken according to the composition, one being used for the determination of nickel and the other for the determination of titanium. Nickel was determined by adding tartaric acid to form the complex with the titanium and then precipitating the nickel with dimethylglyoxime, the precipitate being dried and weighed.

The titanium was determined by evaporating the aliquot to fumes with sulphuric acid and precipitating the titanium from the diluted solution with cupferron, the precipitate being ignited to TiO₂ for weighing.

III.—EXPERIMENTAL RESULTS

The complete equilibrium diagram without experimental points is shown in Fig. 1, whilst Figs. 2(a)–(c) show the diagram in the ranges 0–40, 40–70, and 70–100 at.-% titanium, respectively, together with

* In general this was alumina from the refractories.

data points for the alloys examined. The results of the thermal analyses are summarized in Table II, but tables of exact composition and microstructures are not published because it is felt that the diagrams indicate the positions of the solubility curves to within the limits of the experimental accuracy.

1. THE LIQUIDUS CURVE

The results of the cooling and heating curves are summarized in Table II, and the following points may be noted. The freezing point of nickel is lowered

ture was confirmed by quenching experiments which placed the temperature between 1115° and 1120° C.

The primary arrests for alloys near to the eutectic were weak, and the eutectic composition was determined from the microstructures of slowly cooled and stirred ingots, which showed the presence of primary Ni_3Ti in alloy 37.94 and of NiTi in alloy 39.09.* From this point, the liquidus rises to a second maximum at the equiatomic composition (NiTi) and 1310° C., as compared with the value 1240° C. given by Margolin, Ence, and Nielsen.⁴ The low value obtained by the latter was probably due partly to impurity and partly to an experimental method in which, on heating to

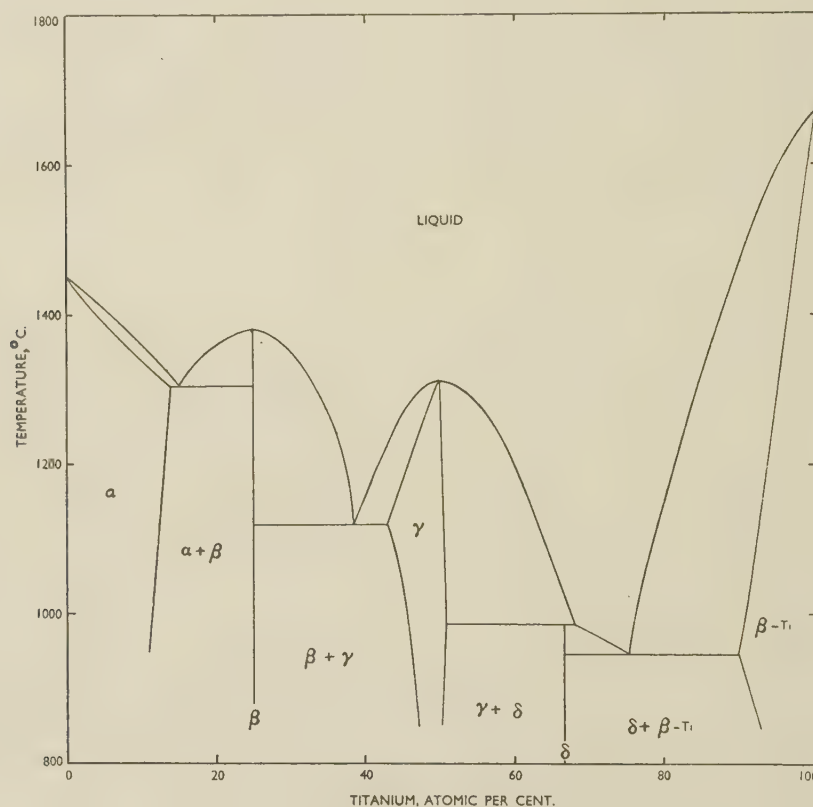


FIG. 1.—The Nickel-Titanium Equilibrium Diagram above 850° C.

markedly by the addition of titanium, and the liquidus curve sinks to a eutectic point at 15.0 at.-% nickel and 1304° C., as compared with the value 1287° C. given by Wallbaum.² The present quenching experiments placed the horizontal between 1303° and 1305° C. The higher values for this and for the later points in the present diagram are undoubtedly due to greater purity of the metals. The liquidus then rises to a round maximum at 25 at.-% titanium (Ni_3Ti) and 1380° C. (Wallbaum 1378° C.), and sinks to 1118° C. (Wallbaum 1100° C.), the temperature of the ($\text{Ni}_3\text{Ti} + \text{NiTi}$) eutectic. The eutectic tempera-

successive temperatures, an alloy was assumed to be totally liquid if it was found to have taken on the shape of the containing graphite crucible, whereas this might well happen while some solid phase remained unmelted.

With increasing titanium content, the liquidus falls steeply to 68 at.-% titanium and 984° C., which is the temperature of the peritectic reaction ($\text{liquid} + \text{NiTi} \rightleftharpoons \text{NiTi}_2$); microscopical and quenching methods placed the peritectic horizontal between 982° and 987° C. The compound NiTi_2 is in equilibrium with the liquid over only a short range of temperature,

* These compositions are indicated by arrows in Fig. 2(b).

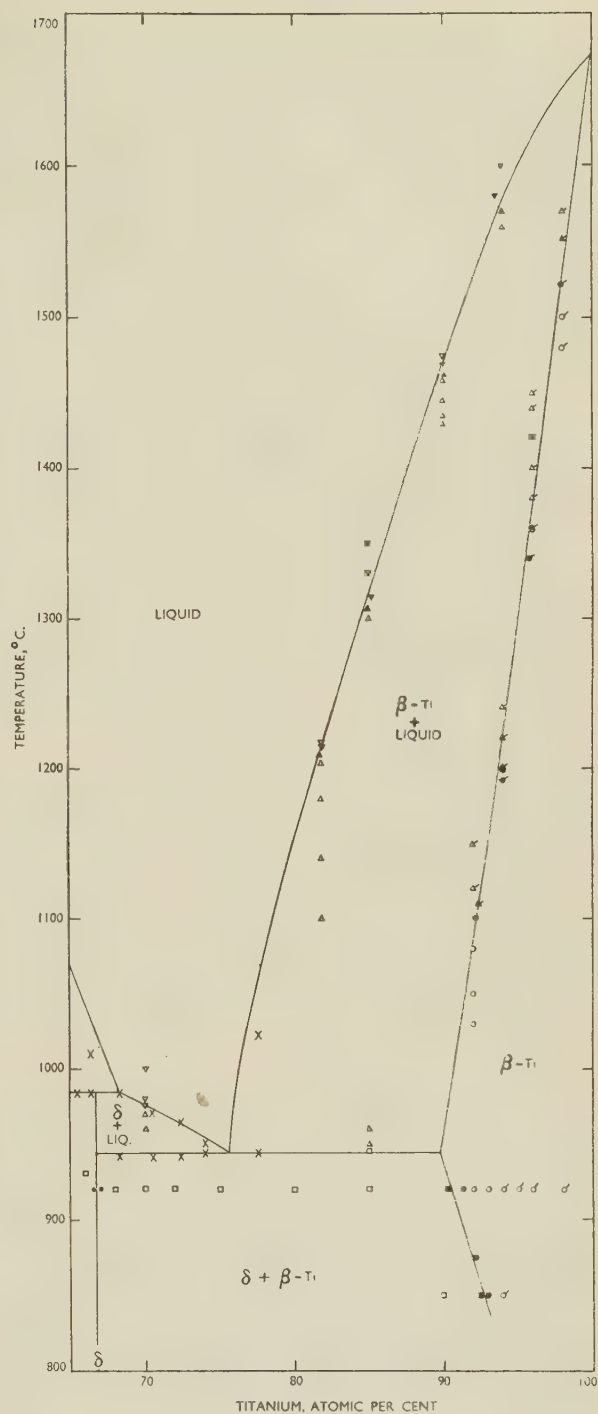
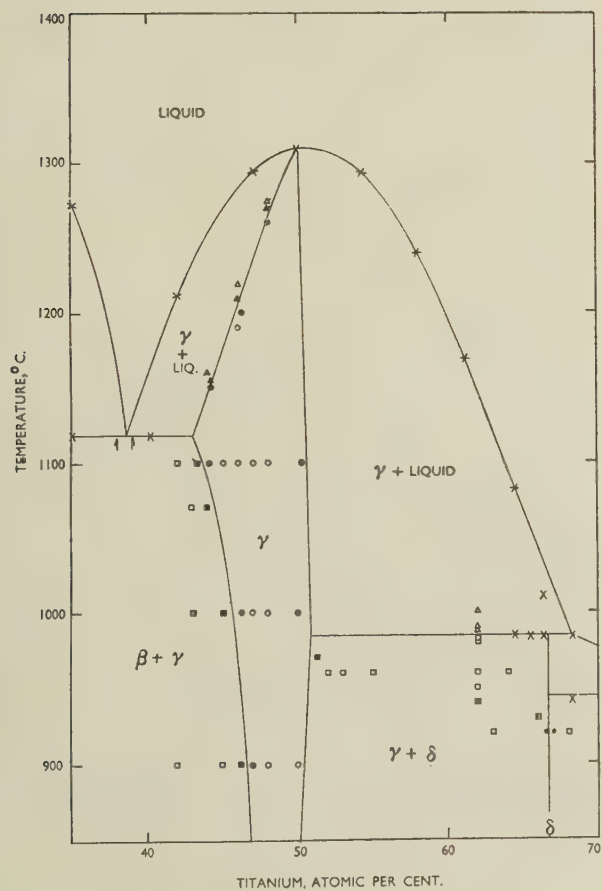
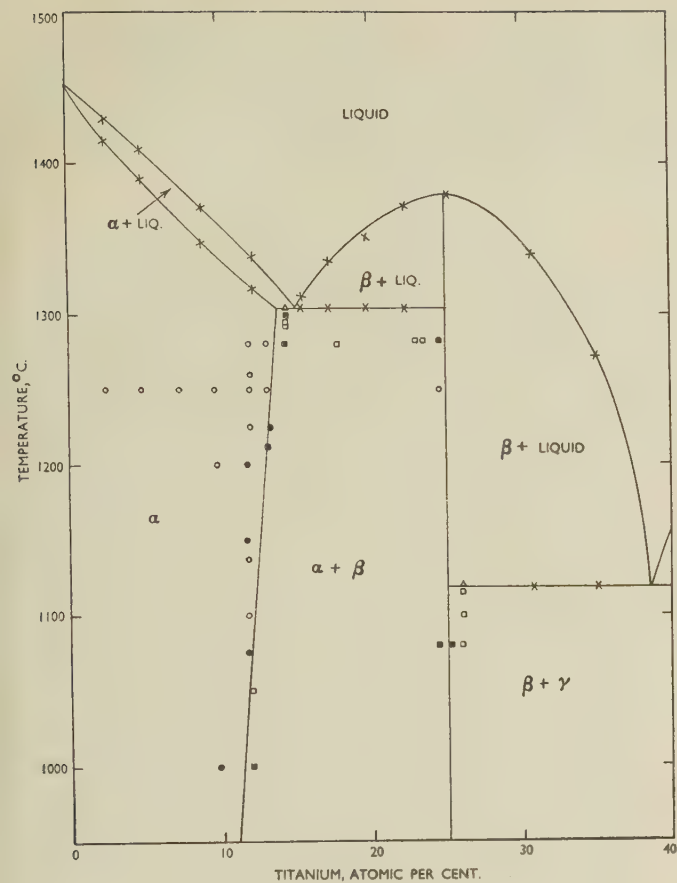


FIG. 2(a)-(c).—The Equilibrium Diagram of the System Nickel-Titanium.

KEY TO FIG. 2.

○ One phase. ▽ Totally liquid. × Thermal arrest.
 □ Two phases. Δ Liquid + solid.

Full points denote analysed alloys.
 Ticks (thus δ) denote decomposed alloys.

and the liquidus falls to 942° C. and 75.5 at.-% titanium, at which the (NiTi₂ + β -Ti) eutectic separates. According to Margolin, Ence, and Nielsen,⁴ the peritectic and eutectic temperatures for NiTi₂ are 1015° and 955° C., respectively, and we can offer no explanation of these higher values.

TABLE II.—*Results of Thermal Analyses.*

Titanium, at.-%	Temperature, °C.			
	Liquidus	Solidus	Eutectic	Peritectic
2.49	1429	1415 *
4.92	1410	1390 *
8.86	1371	1348 *
12.26	1339	1317 *
15.41	1312	...	1304	...
			1305 *	...
17.72	1336	...	1305	...
19.76	1351	...	1305	...
22.28	1372	...	1304	...
25.23	1380
	1380 *
30.74	1342	...	1118	...
35.06	1272	...	1118	...
			1119 *	...
			1118 *	...
40.19	1273
42.03	1211
47.11	1294
49.79	1310
54.34	1294
	1295 *
58.00	1241
61.21	1169
64.48	1082
	1084	985
65.5 †	984
66.39	1011
	1009	984
68.26	984	...	942	...
			942 *	...
70.52	971	...	941	...
			940 *	...
72.41	965	...	942	...
74.00	951	...	944	...
77.57	1023	...	944	...

* Heating curve.

† Not analysed.

The NiTi₂ liquidus was also determined by the microscopical method of Hume-Rothery and Poole.⁹ The application of the method was difficult, because the Ni₂Ti formed star-shaped crystals which could not always be clearly distinguished from the chilled liquid. In spite of this, the liquidus determined by the microscopical method * was within a few degrees of that indicated by the cooling curves. The liquidus then rises steeply to the freezing point of titanium, and is slightly concave towards the temperature axis at pure titanium.

2. THE SOLIDUS CURVES

The solidus points obtained from heating curves for the nickel-rich solid solution are also given in Table II, and should be accurate to within $\pm 1\frac{1}{2}$ ° C. so far as

the pyrometry is concerned. The results obtained by quenching methods for the nickel-rich solidus of the NiTi phase, and for the β -titanium phase are given in Figs. 2(a) and (b), respectively.

3. THE MELTING POINT OF TITANIUM

Until quite recently most American authors gave the melting point of pure titanium as 1725° C., but values between 1680° and 1696° C. have been given in some later papers.¹⁴⁻¹⁶ Work by Schofield and Bacon¹⁷ gave the appreciably lower value of 1660° \pm 10° C., which was based on observations that melting had begun in a sample heated at 1670° C., but not in one heated at 1660° C. As these later results were not at the time available to the present authors, a redetermination of the melting point of titanium was attempted by observing lumps of titanium heated in a container of molybdenum in the furnace used for determining the liquidus by the microscopical method. No melting was observed on heating at 1660° C. or in one experiment at 1680° C.; in a second experiment at 1680° C. signs of melting were apparent, but unfortunately the furnace failed before melting was definitely established. In this work a vacuum of better than 0.02 μ was maintained during the whole experiment. The calibration of the thermocouple against the nickel point did not change by more than 2° C. during the course of an experiment, and from the uncertainty in the e.m.f./temperature curve above 1600° C., the temperature measurements may be regarded as accurate to within ± 8 ° C.† The present work confirms that the true melting point of titanium is appreciably lower than the early value of 1725° C., and slightly higher than the value of 1660° C. given by Schofield and Bacon, but could be reconciled with Schofield's later value of 1665° C.,¹⁸ and the diagrams are drawn to agree with a value of 1672° C.

It is to be noted that titanium is one of the few metals whose melting point is raised by the common impurities (oxygen and nitrogen).

4. THE NICKEL-RICH α SOLID SOLUTION

The points for the solidus curve of the solid solution in nickel lie on a smooth curve which reaches a maximum of 13.8 at.-% titanium at the eutectic temperature. Below this temperature the nickel/(Ni + Ni₃Ti) solubility curve was determined by annealing experiments extending up to 500 hr. at temperatures between 1050° and 1300° C. According to this work, the solubility curve is a straight line falling from 13.8 at.-% titanium at 1304° C. to 11.4 at.-% titanium at 1000° C. This is in good agreement with the boundary proposed by Taylor and Floyd,³ who used the lattice-parameter method based on 24-hr. anneals of the filings of two-phase alloys. This form of solubility curve is theoretically improbable, and the

* The microscopical method was used before thermal analysis had been attempted for these alloys.

† This figure is based on information supplied by Messrs. Johnson, Matthey and Co., Ltd., the makers of the thermocouple wires.

lattice spacing/composition relations for homogeneous alloys were therefore redetermined, with the following results:

Titanium, at.-%	a , kX units at 20° C.
2.29	3.5245
4.28	3.5317
6.15	3.5372
9.36	3.5496

A two-phase alloy, after preliminary treatment at 1280° C., was lump-annealed for 7 days at 1050° C., and was then quenched and used for the preparation of filings which were strain-annealed for 1 hr. at 1050° C., and quenched. The lattice spacing of the nickel-rich solid solution indicated a solubility of 11.7 at.-% titanium, in agreement with the microscopical work. The filings were then re-annealed for 7 days at 1050° C., and the parameter value indicated a solubility of 10.2 at.-% titanium. It is probable, therefore, that the true solubility curve would show a greater decrease at low temperatures than the straight line in Fig. 2(a), although the latter represents the structures found after annealing for 500 hr. at 1050° C.

5. THE Ni_3Ti (β) PHASE

The annealing experiments showed that the homogeneity range of this phase is less than 1 at.-%, but the extreme brittleness of the compound prevented a closer bracket. The points in Fig. 2(a) are based on annealing treatments extending from 4 hr. at 1282° C. to 24 hr. at 1080° C.

An X-ray powder photograph of excellent quality was obtained from a cooling-curve ingot, the ground alloy receiving a strain-relieving anneal of 2 hr. at 1280° C. The indexing of the lines agreed with that given by Taylor and Floyd,³ and when referred to the large unit cell of Duwez and Taylor⁶ the results were:

$$\left. \begin{array}{l} a = 5.0985(5) \pm 0.00005 \text{ kX} \\ c = 8.3019(7) \pm 0.00008 \text{ kX} \\ c/a = 1.6283 \end{array} \right\} \begin{array}{l} \text{at } 25^\circ \text{ C. for a sample from an} \\ \text{ingot which analysis showed to} \\ \text{contain } 25.23 \text{ at.-% Ti.} \end{array}$$

6. THE NiTi (γ) PHASE

The composition limits of the NiTi phase are shown in Fig. 2(b), the points being based on annealing treatments ranging from 24 hr. at 1100° C. to 11 days at 900° C. On the nickel-rich side the limit of this phase falls smoothly from 43.0 at.-% titanium at 1118° C. to 46.6 at.-% at 900° C. On the titanium-rich side, the boundary is very steep, although the range of homogeneity diminishes with falling temperature as indicated by X-ray and microscopical examination of 50 at.-% alloys annealed at 600° C. On the nickel-rich side, the present results near to the eutectic temperature resemble those of Margolin, Ence, and Nielsen,⁴ but the narrowing of the solubility range at lower temperatures appears to be much more pronounced than these workers suggested, whilst on the titanium-rich side the present solubility curve is much nearer to the exact equiatomic ratio.

Filings from a 50 at.-% titanium alloy were annealed at 1000° C., and quenched into silicone oil contained in a long, argon-filled, silica tube. The X-ray-diffraction film from these showed 17 slightly diffuse lines, of which eight were identified as indicating a structure of the CsCl type, with $a = 3.0070 \pm 0.0005$ kX at 22° C. Filings annealed in the same way and rapidly cooled by withdrawing the container from the furnace gave a diffuse X-ray pattern with many lines not attributable to the CsCl type of structure. Filings annealed for 2 weeks at 600° C. showed very diffuse CsCl-type reflections, together with four extra lines which could be attributed to NiTi_2 , and five extremely faint lines which were identified with those of Ni_3Ti . The diffuse nature of the lines suggested that the equilibrium had not yet been obtained, but the appearance of lines characteristic of both NiTi_2 and Ni_3Ti confirms the conclusion of Duwez and Taylor⁶ that NiTi undergoes a low-temperature decomposition into $\text{NiTi}_2 + \text{Ni}_3\text{Ti}$. It is probable, however, that in the rapidly cooled equiatomic alloy the phases present are a partly decomposed CsCl-type phase with precipitated NiTi_2 .

7. THE NiTi_2 (δ) PHASE

The microstructures of the alloys * containing 66 and 68 at.-% Ti showed the presence of excess NiTi and β -titanium respectively, and suggested that the NiTi_2 phase has only a very slight range of composition. The extreme brittleness of the phase prevented the establishment of exact limits.

An X-ray powder photograph of alloy 66.7 * gave a pattern of 50 lines, which, in agreement with Duwez and Taylor⁶ could be indexed as belonging to a cubic structure with $a = 11.297 \pm 0.002$ kX at 21° C.

8. THE β -TITANIUM SOLID SOLUTION

The $\beta\text{-Ti}/(\beta\text{-Ti} + \text{NiTi}_2)$ boundary shown in Fig. 2(c) was determined by annealing experiments varying in duration from 1 day at 920° C. to 7 days at 850° C. At the eutectic temperature the limit of the solid solution extends to 89.7 at.-% Ti, which is in agreement with the values of 89.1 and 90 at.-% titanium proposed by Margolin *et al.*⁴ and by Long *et al.*⁸ at 955° and 960° C., respectively, although the boundary proposed here lies wholly on the nickel-rich side of those proposed by Margolin *et al.* and by Long *et al.*

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* These alloys were not analysed, because the weights of the arc-melted ingots agreed well with those of the metals melted,

whilst the analysis of other arc-melted alloys showed that the desired composition was obtained within a few tenths per cent.

REFERENCES

1. A. D. McQuillan, *J. Inst. Metals*, 1951-52, **80**, 363.
2. R. Vogel and H. J. Wallbaum, *Arch. Eisenhüttenwesen*, 1938-39, **12**, 299.
H. J. Wallbaum, *ibid.*, 1940-41, **14**, 521.
3. A. Taylor and R. W. Floyd, *Acta Cryst.*, 1950, **3**, 285.
A. Taylor and R. W. Floyd, *J. Inst. Metals*, 1951-52, **80**, 577.
4. H. Margolin, E. Ence, and J. P. Nielsen, *Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197**, 243.
5. F. Laves and H. J. Wallbaum, *Naturwiss.*, 1939, **27**, 674;
Z. Krist., 1939, **10**, 78.
6. P. Duwez and J. L. Taylor, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, **188**, 1173.
7. W. Rostoker, *ibid.*, 1951, **191**, 1203.
8. J. R. Long, E. T. Hayes, D. C. Root, and C. E. Armantrout, *U.S. Bur. Mines, Rep. Invest.*, 1949, (**4463**).
9. W. Hume-Rothery and D. M. Poole, *J. Inst. Metals*, 1953-54, **82**, 490.
10. G. B. Harris and W. Hume-Rothery, *J. Iron Steel Inst.*, 1953, **174**, 212.
11. W. Hume-Rothery, J. W. Christian, and W. B. Pearson, "Metallurgical Equilibrium Diagrams". 1952: London (Institute of Physics).
12. W. B. Pearson and W. Hume-Rothery, *J. Inst. Metals*, 1951-52, **80**, 641.
13. F. M. Cain, Jr., *Zirconium and Zirconium Alloys* (Amer. Soc. Metals), 1953, 176.
14. H. R. Ogden, D. J. Maykuth, W. L. Finlay, and R. I. Jaffee, *Trans. Amer. Inst. Min. Met. Eng.*, 1951, **191**, 1150.
15. H. K. Adenstedt, J. R. Pequignot, and J. M. Raymer, *Trans. Amer. Soc. Metals*, 1952, **44**, 990.
16. D. J. Maykuth, H. R. Ogden, and R. I. Jaffee, *Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197**, 225.
17. T. H. Schofield and A. E. Bacon, *J. Inst. Metals*, 1953-54, **82**, 167.
18. T. H. Schofield, *Proc. Phys. Soc.*, 1954, [B], **67**, 845.

THE SOLID SOLUBILITY OF CHROMIUM CARBIDE, Cr_3C_2 , IN TITANIUM CARBIDE *

1624

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SYNOPSIS

X-ray-diffraction methods show that TiC dissolves up to 51 wt.-% Cr_3C_2 at 1725° C., the temperature of maximum solubility. The solubility falls rapidly with decrease in temperature, being only about 4% at 1300° C. The remainder of the TiC- Cr_3C_2 pseudo-binary diagram has been explored in outline by metallographic and X-ray-diffraction techniques. The system is of a simple eutectic type, and the eutectic composition and temperature have been found to be about 4% TiC and 1725° C., respectively. No evidence of any solid solubility of TiC in Cr_3C_2 has been obtained.

I.—INTRODUCTION

THE solid solubility of chromium carbide, Cr_3C_2 , in titanium carbide, TiC, was previously investigated to some extent by Mol'kov and Vikker,¹ who found that the solubility limit at 1600° C. was less than 70 wt.-% Cr_3C_2 and at 1000° C. less than 40 wt.-% Cr_3C_2 . No lattice-parameter measurements were published, and the X-ray-diffraction films were examined visually. In the present work, accurate determinations of the solid solubility by X-ray-diffraction and metallographic techniques, over the temperature range 1250°–1900° C., are reported. In addition, the remainder of the pseudo-binary system TiC- Cr_3C_2 has been explored in outline by metallographic methods.

A solid solution of Cr_3C_2 in TiC constitutes the carbide phase in two series of commercial sintered alloys.^{2,3} Chromium carbide is a particularly useful alloy addition for nickel- or cobalt-bonded TiC alloys, since, if sufficient is added, the TiC phase becomes saturated with Cr_3C_2 , and any excess dissolves in the bond. In this manner, the oxidation-resistance of both the carbide and the metal phases is increased, and so is the creep-resistance of the metal phase.

II.—PREPARATION OF TITANIUM AND CHROMIUM CARBIDES

The TiC used in this investigation was produced by heating the appropriate mixture of titanium dioxide and lamp-black in a carbon-tube resistance furnace at 2150° C. in a protective atmosphere of pure dry hydrogen. The resultant carbide was ball-milled for a short period and sieved through a 200-mesh B.S.S. sieve. Chemical analysis gave total carbon 19.60, free carbon 0.20, and tungsten 0.57%. The tungsten content was low, indicating that little tungsten carbide had been picked up from the cemented tungsten

carbide balls used in the ball-milling, and was insufficient to cause any appreciable errors in subsequent lattice-parameter determinations. Qualitative spectrographic analysis showed the presence of very small traces of impurities. The lattice parameter of the face-centred cubic cell was found to be 4.3183 ± 0.001 kX units.

Cr_3C_2 was prepared by heating the appropriate mixture of chromic oxide and lamp-black in pure dry hydrogen at 1650° C. in a carbon-tube resistance furnace. The carbide was ball-milled and sieved in the same manner as the TiC; subsequent chemical analysis gave: total carbon 13.40% (theoretical 13.33%), tungsten 0.20%. The pick-up of tungsten carbide was again small.

The X-ray powder photograph showed the presence of Cr_3C_2 only, the lattice parameters of the orthorhombic cell being: $a = 2.82$, $b = 5.52$, and $c = 11.46$ kX.

Mixtures of titanium and chromium carbides were made by ball-milling the required proportions of the carbides together for 24 hr. These mixtures were made up in 500-g. batches.

III.—EXPERIMENTAL PROCEDURE

The solid solubility of Cr_3C_2 in TiC was determined by heating pressed compacts of the mixed carbides at various temperatures, and examining the compacts after rapid cooling. The mixed carbides, pressed into compacts 2 cm. square and 0.5 cm. thick, were placed in thin-walled graphite crucibles which lay end to end in a thin-walled graphite boat in a carbon-tube resistance furnace, in a hydrogen atmosphere. The end graphite crucible was fitted with a deep hollow lid, upon which a pyrometer of the disappearing-filament type was sighted. The temperature of this end crucible could be measured under good black-body conditions, and as the graphite boat was short in length,

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compared with the constant-temperature zone of the furnace, the temperature of all the graphite crucibles was substantially the same. The compacts were held at temperature for the necessary time, and then the graphite boat was pushed quickly into the water-cooled zone of the furnace tube and allowed to cool. The cooling rate was very rapid, the compacts cooling from, say, 1800° to about 700°C . in about 30 sec. Fragments of the compacts were crushed in a cemented tungsten-carbide-lined percussion mortar to pass a 200-mesh B.S.S. sieve for taking the X-ray powder photographs, and sections of selected compacts were ground and polished for metallographic examination.

The X-ray photographs were taken with powder cameras 14.3 cm. in dia., fitted with knife edges so that reflections up to a Bragg angle of 82° could be observed. The powders were coated on glass filaments mounted in accurately centred bushes. Accurate values of the lattice parameter were obtained by the method advocated by Lipson and Wilson.⁴ Unfiltered cobalt radiation was used. The background on powder films taken of alloys containing above about 30% Cr_3C_2 was heavy, and in the case of some films this prevented highly accurate results being obtained. At the time, however, this radiation was the best available.

The remainder of the pseudo-binary system TiC- Cr_3C_2 was explored by heating pressed compacts of several compositions at various temperatures, and examining the alloys after both slow and rapid cooling. If the slowly cooled condition was required, the compacts were allowed to cool in the furnace. Compacts of all compositions were examined by X-ray and metallographic methods. Chromium radiation was used with the alloys containing above about 60 wt.-% Cr_3C_2 .

IV.—EXPERIMENTAL RESULTS

Preliminary experiments showed that heating the compacts of mixed carbides for only 1 hr. at 1250°C . was sufficient to effect complete diffusion, and this annealing period was therefore adopted for all temperatures. These experiments also showed that the rate of cooling was sufficiently rapid to avoid any decomposition of the solid solution during cooling.

The lattice parameters of the TiC phase in the compacts quenched from various temperatures are shown in Fig. 1. The temperatures quoted are those measured with the optical pyrometer, to which a correction has been applied for the transmission of the furnace window.⁵ The lattice parameters are plotted against the analysed compositions (molecular percentage of Cr_3C_2), and at all temperatures the lattice parameter/composition curve consists of two distinct parts, the first approximately linear and the second horizontal, representing a constant TiC phase composition. The first part represents the lattice parameter/composition curve for single-phase alloys, and Vegard's law is approximately obeyed. The solubility limit at each temperature was determined by the point of intersec-

tion of the two parts of the curve, and these solubility limits are shown in Fig. 2.

Measurements of the reflection intensities were not made, but visual inspection revealed no differences in corresponding reflection intensities between the diffraction patterns from the solid solutions and those from the parent TiC.

Fig. 2 also gives the results of the investigation of the remainder of the pseudo-binary system. In the whole range of alloys, only two phases were detected, the TiC-rich and Cr_3C_2 -rich phases. No additional phase was detected by qualitative X-ray powder photographs.

The metallographic examination of TiC-rich alloys heated below about 1600°C . was difficult, as the com-

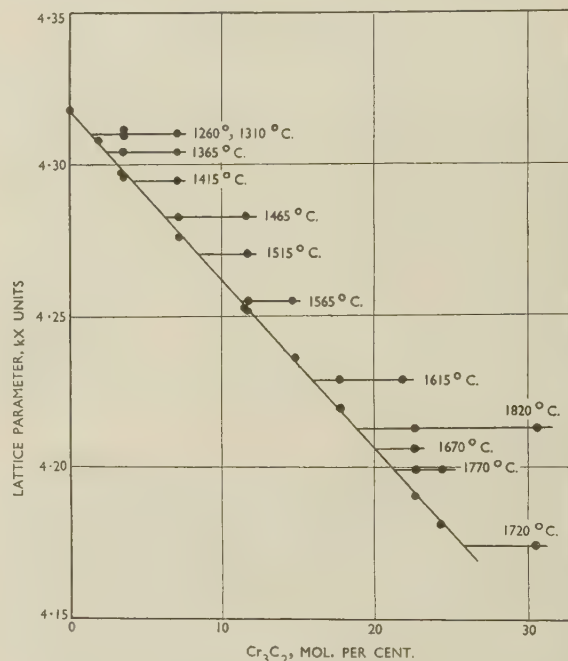


FIG. 1.—Lattice Parameters of TiC Phase at Various Temperatures.

pacts were very porous. The structure of a typical two-phase TiC-rich alloy is shown in Fig. 3 (Plate LXX) in which the excess Cr_3C_2 can be seen segregated in the grain boundaries of the TiC-base solid solution. Two-phase TiC-rich alloys heated above 1725°C . were blistered and distorted after cooling, indicating that liquid phase had been present during heating. The alloys containing less than 50% TiC, heated in the liquid + TiC field above 1725°C ., contained TiC-rich solid solution and fine eutectic after cooling.

A few alloys, containing 3, 4, and 5% TiC, were examined after slow cooling from 1770°C . in order to confirm the eutectic composition. The 4% TiC alloy consisted entirely of coarse eutectic (Fig. 4, Plate LXX). Compacts of pure Cr_3C_2 were unchanged after heating to 1830°C ., but became completely liquid on heating to 1930°C .

X-ray powder films obtained from rapidly cooled Cr_3C_2 -rich alloys were examined to determine whether or not the Cr_3C_2 had dissolved any TiC , but no "shift" was observed in the diffraction pattern of the Cr_3C_2 .

V.—DISCUSSION OF RESULTS

The X-ray and metallographic results show that the solid solubility of Cr_3C_2 in TiC reaches a maximum of 51 wt.-% at 1725°C ., but below 1725°C the solubility

The X-ray and metallographic results on the remainder of the alloys show that TiC and Cr_3C_2 form a simple eutectic pseudo-binary system, with extensive solid solubility at the TiC -rich end, and with very limited or no solid solubility at the Cr_3C_2 end. No intermediate constituent was observed, by either metallographic or X-ray methods. Pure TiC melts at about 3150°C .,⁶ and is formed directly from the melt. The mode of formation of Cr_3C_2 appears to be in doubt. Most diagrams, including that by Sykes,⁷

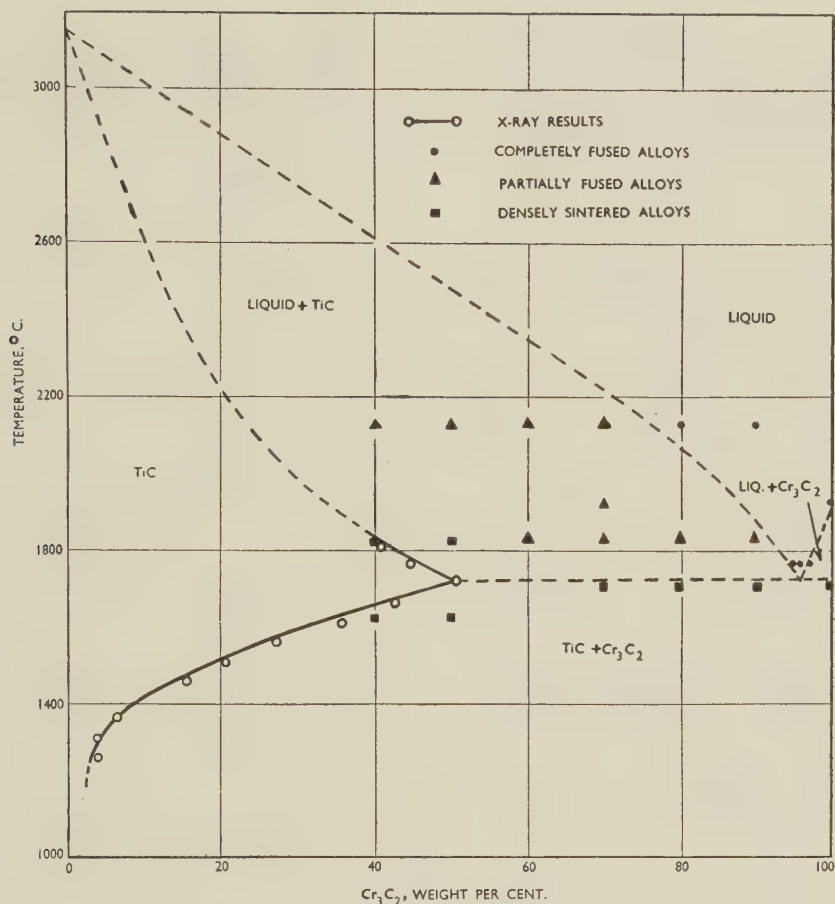


FIG. 2.—Equilibrium Diagram of Pseudo-Binary $\text{TiC}-\text{Cr}_3\text{C}_2$ System.

decreases rapidly with fall in temperature and at 1300°C it is only about 4%. Above 1725°C the solubility decreases with increase in temperature, and since the structure of two-phase alloys heated above 1735°C suggested that liquid phase had been present, the solid-solubility curve above 1725°C is the solidus of the $\text{TiC}-\text{Cr}_3\text{C}_2$ system. Visual inspection of the powder films revealed no differences in the reflection intensities between powder films of pure TiC and those of the solid solutions; consequently the structure of the TiC is not changed by solution. Presumably some carbon sites in the solid-solution lattice are vacant; the presence of vacant carbon sites in pure titanium carbide has been previously observed.⁶

show that Cr_3C_2 forms directly from the melt at about 1820°C ., but a more recent diagram by Bloom and Grant,⁸ who used materials of greater purity, shows that Cr_3C_2 melts at 1895°C ., but is formed as a result of a peritectic reaction and not directly from the melt. No experimental evidence is quoted to support the existence of this peritectic reaction, and in the present work it is assumed that Cr_3C_2 forms directly from the melt.

TiC and Cr_3C_2 form a eutectic at about 4% TiC . The eutectic temperature is found to lie between 1710° and 1770°C from the metallographic evidence, and the temperature of maximum solid solubility of Cr_3C_2 in TiC is established as 1725°C from the X-ray results.

The maximum solid solubility of Cr_3C_2 in TiC is compared below with the solid solubilities in TiC of Mo_2C and WC, the carbides of other Group VI metals.

Carbide	Max. Solubility, wt.-%	Temp., °C.
Cr_3C_2 .	51	1725
Mo_2C ⁹	97	2600
WC ¹⁰	95.5	2450

The solid solubility decreases rapidly below 1725° C. and is only about 4% at 1300° C. This low solid-solubility limit is of importance in the manufacture of heat- and creep-resistant alloys based on a solid solution of Cr_3C_2 in TiC, as some of these alloys are sintered at temperatures around 1300° C. In such an alloy any Cr_3C_2 in excess of the solubility limit will exist in solution in the nickel or cobalt bond, or, if there is a large excess, free Cr_3C_2 will be present.

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REFERENCES

1. L. P. Mol'kov and I. V. Vikker, *Vestn. Metalloprom.*, 1936, **16**, (6), 75.
2. E. M. Trent, A. Carter, and J. Bateman, *Metallurgia*, 1950, **42**, 111.
3. R. Kieffer and F. Kölbl, *Z. anorg. Chem.*, 1950, **262**, 229.
4. H. Lipson and A. J. C. Wilson, *J. Sci. Instruments*, 1941, **18**, 144.
5. —, *British Standard No. 1041*, (1943), pp. 37–40.
6. P. Schwarzkopf and R. Kieffer, "Refractory Hard Metals". 1953: New York (The Macmillan Company).
7. W. P. Sykes, *Metals Handbook (Amer. Soc. Metals)*, 1948, 1181.
8. D. S. Bloom and N. J. Grant, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, **188**, 41.
9. Ya. S. Umansky, *Izvest. Sekt. Fiziko-Khim. Anal., Inst. Obshch. Neorg. Khim. Akad. Nauk S.S.S.R.*, 1943, **16**, (1), 127.
10. A. G. Metcalfe, *J. Inst. Metals*, 1947, **73**, 591.

A STUDY OF THE TITANIUM-GERMANIUM SYSTEM 1625

IN THE REGION 0-11 ATOMIC PER CENT.

GERMANIUM*

By (Mrs.) M. K. McQUILLAN, † M.A., MEMBER

SYNOPSIS

The system titanium-germanium has been examined by micrographic methods in the range 0-11 at.-% germanium, at temperatures from 500° to 1500° C. Germanium is found to cause a slight elevation of the transformation temperature of titanium, a peritectoid reaction in which β -titanium reacts with the compound Ti_5Ge_3 to form α -titanium occurring at $897^\circ \pm 3^\circ$ C. The compound Ti_5Ge_3 is formed from the melt by a eutectic reaction at $1410^\circ \pm 10^\circ$ C.

Anomalous structures have been observed as a result of heating as-cast alloys in the ($\alpha + Ti_5Ge_3$) region. Their origin is discussed.

I.—INTRODUCTION

THE preliminary stages of an investigation directed towards the elucidation of the fundamental principles underlying the alloying behaviour of titanium have involved studies of the constitution of several titanium alloy systems concerning which little information has hitherto been available. The titanium-germanium system is one of these. Alloys containing up to 10.8 at.-% germanium have been studied by micrographic methods in the range 500°-1500° C.

II.—EXPERIMENTAL PROCEDURE

1. PREPARATION OF THE ALLOYS

The alloys were made from iodide titanium of the highest available purity. Examination of the material by the hydrogen-pressure method indicated that its transformation range was 872°-880° C., and that it contained an unusually low concentration of interstitial impurities. The only impurities revealed by chemical and spectrographic analysis were zirconium of the order of 0.5 at.-% and 0.025 at.-% iron. The presence of zirconium was considered to be less objectionable than the higher concentration of the interstitial elements, oxygen, nitrogen, and carbon, contained by all the other samples of iodide titanium examined. The hardness of the material was 80-85 D.P.N.

The germanium was stated by its suppliers to be of 99.9% purity, and no metallic impurities were detected by chemical and spectrographic analysis.

Ingots weighing 5-6 g. were prepared by the method which has become standard for experimental titanium alloys, i.e. arc-melting on a water-cooled copper hearth under gettered argon at reduced pressure. A control specimen of unalloyed iodide titanium was melted with the alloys to check the melting conditions,

which were accepted as satisfactory only if no increase occurred in the hardness of the control during melting.

Coring appeared in the as-cast alloys, but no major inhomogeneities were observed. Comparison between the combined weight of the alloy constituents and that of the melted ingot indicated that some loss usually occurred during the melting process, particularly at the higher germanium contents. This was presumed to be due to loss of germanium by volatilization. Compositions calculated on the assumption that all observed weight losses were germanium, are compared with the analysed compositions in Table I.

TABLE I.—Comparison between Nominal, Calculated, and Analysed Compositions of the Titanium-Germanium Alloys.

Nominal Composition, at.-% Ge	Calculated Composition Allowing all Weight Loss as Germanium, at.-%	Analysed Composition, at.-% Ge
1	0.87	0.89
2	1.88	1.95
3	3.01	2.97
4	3.98	3.87
5	4.98	5.05
6	6.00	6.03
7	6.98	7.13
7.5	7.19	7.22
7.5	7.48	7.40
8	7.88	... *
9.15	9.11	... *
8.5	8.51	8.28
10	9.38	9.38
12	10.86	10.66

* Insufficient material available for accurate analysis.

2. HEAT-TREATMENT

Three different methods were adopted, depending on the temperature and duration of the heat-treatment

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† Imperial Chemical Industries, Ltd., Metals Division, Birmingham. 485

in question, on the rate of cooling required, and on the number of specimens to be heated.

For brief heat-treatments involving small numbers of specimens, and whenever rapid quenching was necessary, a vacuum-quenching apparatus of the type described in an earlier paper¹ was used. In this apparatus the specimens are supported on a platinum/platinum-rhodium thermocouple in the space between two metal-strip heaters, arranged in the form of a bow. On completion of the heat-treatment, a jet of water is allowed to impinge upon the specimen by opening a vacuum tap connected to a water reservoir, the power supply to the heaters being cut off simultaneously. This procedure ensures an almost instantaneous quench.

Below 1000° C. titanium heater strips were employed, the advantage of these being not only that all risk of metallic contamination is thereby avoided, but also that their gettering action prevents any contamination by residual gases. At higher temperatures, molybdenum heaters were used. The maximum temperature at which titanium-germanium specimens could be heated in the vacuum-quenching apparatus was about 1350° C., owing to the beginning of reaction between the specimens and the thermocouple. Heater life was the limiting factor in heat-treatment duration, but this was not a serious disadvantage, since prolonged heat-treatments at high temperatures in the vacuum-quenching apparatus were in any case avoided, owing to the possible danger of slow gas pick-up in the absence of any gettering mechanism.

When groups of specimens were to be subjected to prolonged heat-treatments, conventional tube furnaces were used. Precautions taken to prevent gas contamination involved enclosing the specimens in a stoppered titanium cylinder placed within a heating tube evacuated to a pressure of less than 10^{-5} mm. of mercury. For work below 1000° C., the heating tube was of transparent silica and was enclosed by a similar tube evacuated to a pressure of 5×10^{-3} mm. of mercury, to reduce the possibility of diffusion of gases into the system. Heating tubes for temperatures above the working range of clear silica were either of mullite or recrystallized alumina. No outer vacuum envelope could be used in this case, owing to the small internal diameter of the platinum-wound furnace in which the high-temperature work was carried out.

Since the most reliable precautions against gas contamination are in most cases incompatible with rapid quenching, no attempt was made to quench from the tube furnaces. At the end of a heat-treatment, the heating tube was sealed, removed from the furnace, and allowed to cool in air. When doubt arose concerning possible changes in microstructure during cooling, individual specimens were reheated to the heat-treatment temperature in the vacuum-quenching apparatus for a time sufficient to restore the high-temperature structure and then quenched.

The estimated accuracy of the temperatures recorded is $\pm 2^\circ$ C. for work done in the tube furnaces at

lower temperatures, and $\pm 5^\circ$ C. for specimens heated in the vacuum-quenching apparatus or at high temperatures in a tube furnace.

The duration of the heat-treatments was determined by the observed behaviour of individual specimens and by the type of furnace used. In general, heat-treatments in the platinum-wound tube furnace in the range 1300°–1500° C. consisted of a heating-up period of some 6 hr. + 2 hr. at the desired heat-treatment temperature. In the same temperature range, using the vacuum-quenching apparatus, the heating-up period was of the order of a few minutes and the holding time about $\frac{1}{2}$ hr. The fact that consistent results were given by the two different experimental techniques was taken as an indication that equilibrium had been achieved. The heat-treatment times for quenching experiments at lower temperatures were usually about 1 hr. at 1200°–1300° C., 2 hr. at 1000°–1200° C., and 6 hr. at 900°–1000° C., although these times were varied appreciably in order to ascertain whether any given structure was, in fact, an equilibrium structure. Nearly all the work below 900° C. was done in the low-temperature tube furnaces, the vacuum conditions in which were sufficiently good to permit prolonged heat-treatment without any danger of contamination. In the range 750°–900° C., heating periods varying from 16 hr. to 1 week produced closely similar structures, and a duration of 2–3 days was selected for most of the heat-treatments. At 700° C. the maximum heat-treatment time was 1 week, at 640° C. 2 weeks, and at 525° C. 3 weeks, although again shorter periods gave very similar structures at the first two temperatures.

Homogenization of the as-cast alloys presented some problems, since no sufficiently extensive single-phase region, in which a general homogenizing treatment could be carried out, was available in the range 1000°–1200° C., and heat-treatment at higher temperatures in the β phase field, for reasons discussed below, could not be relied upon to produce uniform structures. The slight coring observed in the as-cast alloys was not persistent, however, and was removed either at the heat-treatment temperature by heating the specimens until the structures were uniform, or, when the experimental point in question was close to a phase boundary, by heating the specimen in the adjacent single-phase region before carrying out the final heat-treatment. The alloys containing 1.9 and 3 at.-% germanium, for instance, were cold worked and heated for 3 days at 880° C., as a preliminary to further heat-treatment.

3. ETCHING SOLUTIONS

The primary solid solutions etched satisfactorily in a saturated solution of oxalic acid containing 1% by volume of hydrofluoric acid and a few crystals of ferric nitrate,² but structures which contained an intermetallic compound were seen most clearly after etching in a solution containing 2% nitric acid and 2% hydrofluoric acid.

III.—THE EQUILIBRIUM DIAGRAM

Germanium has been found to be one of the small class of substitutional alloying elements which raise the temperature of the $\alpha \rightarrow \beta$ transformation in titanium. The extent of the effect is, however, limited by a peritectoid reaction at $897^\circ \pm 3^\circ \text{C.}$, the occurrence of which is demonstrated by Figs. 1 and 2 (Plate LXXI), illustrating the structures of a titanium alloy containing 4 at.-% germanium after heating at 900° and 894°C. , respectively. In addition to the small quantity of an intermetallic compound visible in both specimens, the alloy heated at 900°C. shows a matrix of acicular α of the type formed from the β phase on quenching; whereas the specimen heated at 894°C. shows polygonal grains of equilibrium α phase. The intermetallic compound which first appears at a composition just below 2 at.-% germanium at 500°C. and at about 9 at.-% germanium at 1400°C. has been found by X-ray examination to be Ti_5Ge_3 , as described by Pietrowsky and Duwez.³ This same compound is formed from the melt by a eutectic reaction occurring

at $1410^\circ \pm 10^\circ \text{C.}$, as may be seen from Fig. 3 (Plate LXXI), which represents the structure of an alloy containing 10.8 at.-% germanium in the as-cast condition. The eutectic composition, which lies beyond the range of germanium concentration studied,

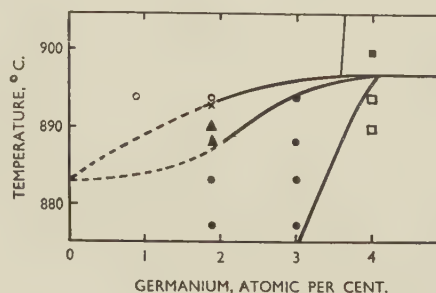


FIG. 8.—Detail of the Titanium-Rich Region of the Titanium-Germanium System.

KEY TO FIGS. 7 AND 8.

- α .
- β .
- ▲ $\alpha + \beta$.
- $\alpha + \text{Ti}_5\text{Ge}_3$.
- $\beta + \text{Ti}_5\text{Ge}_3$.
- ◇ Liquid.
- ◆ Liquid + β .
- × Hydrogen-pressure point.

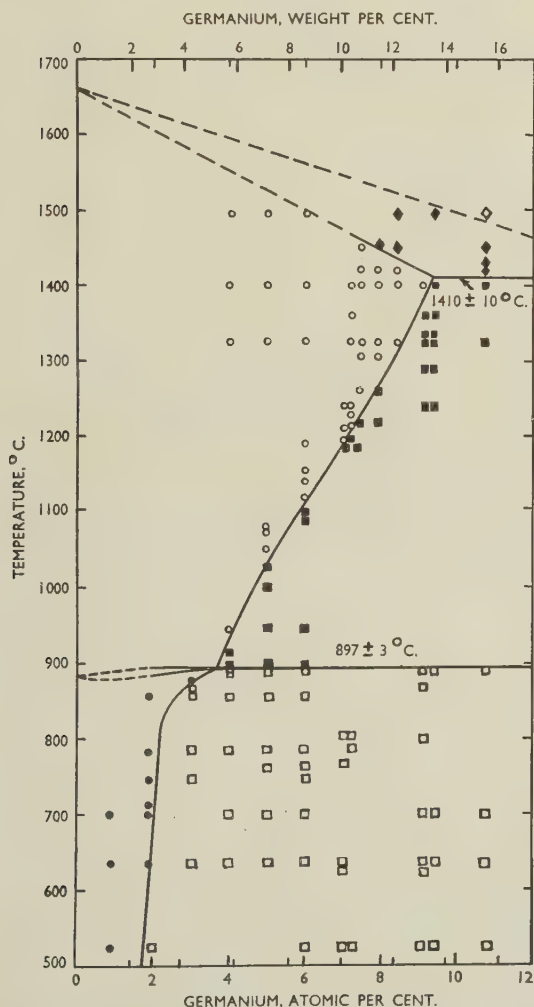


FIG. 7.—The Constitutional Diagram of the Titanium-Germanium System in the Range 0–12 at.-% Germanium.

would be expected, judging from the relative quantities of primary solid solution and eutectic observed in the cast specimens, to be about 16 at.-%. The constitutional diagram determined for the composition range 0–11 at.-% germanium is presented in Figs. 7 and 8.

It was not found possible to retain the β phase at low temperatures even by quenching very rapidly, nor were any structures of the type usually associated with a martensitic transformation observed. The transformed β structures ranged from coarse serrated nucleated α to a fine, regular Widmanstätten array of α platelets, depending on the composition of the alloy and the rate of quenching. The difficulty of distinguishing small quantities of equilibrium α from the coarse serrated α produced by quenching alloys of lower germanium content from the β phase field, caused uncertainty in the location of the $\beta/(\alpha + \beta)$ boundary. A check experiment was therefore carried out on an alloy containing 1.9 at.-% germanium, using the hydrogen-pressure method.⁴

IV.—ANOMALOUS STRUCTURES IN HEAT-TREATED ALLOYS

In fixing the $\alpha/(\alpha + \text{Ti}_5\text{Ge}_3)$ boundary, a series of as-cast alloys containing up to 8 at.-% germanium was heated for periods varying from 16 hr. to a week, at a number of temperatures in the range 500° – 900°C. Initially, these specimens consisted of cored, serrated α resulting from the transformation of the β phase on cooling from the melt, as typified by Fig. 4 (Plate LXXI), which illustrates the structure of an as-cast alloy containing 6 at.-% germanium. During heat-treatment, precipitation of the compound Ti_5Ge_3 occurred in all specimens containing 3 at.-% ger-

manium or more. The appearance of the resultant microstructures, however, did not suggest that the precipitation had occurred in a single-phase alloy of the type shown in Fig. 4, but rather that the alloy had originally consisted of a network of small grains arranged in the boundaries of a large polygonal grain structure. Composition differences between the large grains and the grain-boundary network were indicated by differences in the amount and form of the Ti_5Ge_3 compound observed in the two areas. The type of structure obtained may be seen in Fig. 5 (Plate LXXI), which represents the alloy of Fig. 4 after heating for 3 days at $750^\circ C$. In order to show an area of the specimen sufficiently large to illustrate the intergranular network, it has been necessary to use a low magnification at which it is not easy to observe the precipitated compound clearly, but it will be noted that in the centres of the grains a large quantity of very finely divided compound appears, whereas in the grain-boundary network smaller amounts of compound occur in the form of parallel platelets.

Since no apparent connection existed between the grain structure brought out by the precipitating compound and the observed structure of the alloy before precipitation, some consideration was given to its origin. The possibility that the heat-treatments had been carried out in a region in which two α phases of slightly different composition co-existed, and that the compound had been precipitated during the cooling process, was disproved by experiments which showed conclusively that Ti_5Ge_3 was an equilibrium phase. It seemed, therefore, that the two-phase structure might have developed in the short time during which the alloy was in the β field on cooling from the melt, i.e. that the alloy had passed through a high-temperature ($\beta_1 + \beta_2$) field. Attempts to locate such a two-phase region were hampered by the fact that the β phase could not be retained on cooling, and by the usual experimental difficulties involved in heat-treatments at high temperatures. Some alloys, notably those containing 4-7 at.-% germanium, showed non-uniform precipitation of Ti_5Ge_3 on heating at $800^\circ C$. after cooling from $1325^\circ C$., but the structures, an example of which is shown in Fig. 6 (Plate LXXI), were not of the grain-boundary-network type, and cannot be regarded as affording positive evidence for a two-phase region in the β field. Such a region, if it existed, would have to take the form of a closed loop—a phenomenon not previously observed in metallurgical work. Furthermore, the presence of coring in the as-cast alloys suggests that sufficient diffusion to permit the establishment of a ($\beta_1 + \beta_2$) structure is unlikely to have occurred during cooling through the β phase field.

V.—DISCUSSION

As the second constituent of a binary titanium alloy system, the only other element with which germanium can be compared is tin. Recent work^{6,7} on

titanium-tin alloys indicates, however, that although the transformation temperature of titanium is raised by large additions of tin, small additions depress it, a minimum occurring at about 6 at.-% tin. If such a minimum occurs in the titanium-germanium system it must lie between 0 and 2 at.-% germanium.

The solubility of germanium in both α - and β -titanium is much more restricted than that of tin appears to be. Germanium and tin have size-factors with reference to titanium of -5.4 and $+7.5$, respectively; unless, therefore, both the α and β lattices can accommodate larger atoms more easily than smaller ones (and evidence against this is to be found in other titanium alloy systems), it must be assumed

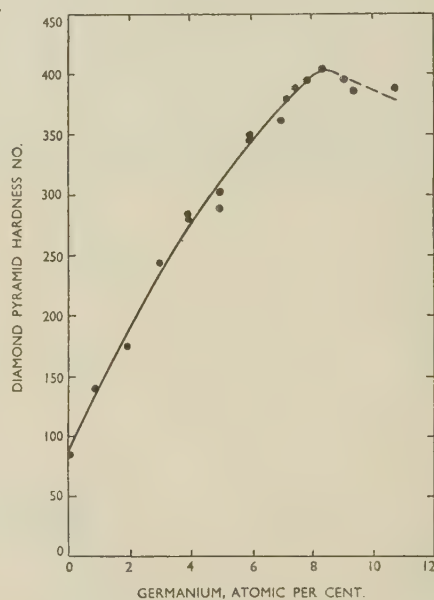


FIG. 9.—Hardness/Composition Relationship for As-Cast Titanium-Germanium Alloys.

that the compound Ti_5Ge_3 is much more stable than the first tin-rich phase appearing in the titanium-tin system. Some support for this view may be found in the observation that no discontinuity occurs in the hardness/composition curve (Fig. 9) for single-phase α alloys, at the composition at which α phase becomes supersaturated; this suggests that lattice strain caused by the dissolution of germanium in α -titanium is not the factor limiting its solubility.

Although the unsatisfactory experimental evidence concerning the anomalous structures observed in some titanium-germanium alloys discourages the development of any hypotheses, it may be mentioned that the existence of a ($\beta_1 + \beta_2$) region at high temperatures would appear to be a reasonable extension of the "clustering" mechanisms proposed to account for the behaviour of the β solid solution in the titanium-chromium alloys.⁵ If the effects observed in the titanium-chromium alloys are electronic in origin and connected with the transformation temperature, they might be expected to occur at

higher temperatures in systems in which the transformation temperature is raised by the addition element, than in systems in which the transformation temperature is depressed.

for identifying the intermetallic compound. Her thanks are also due to Mr. J. R. Lumby for his assistance with the experimental work.

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REFERENCES

1. M. K. McQuillan, *J. Inst. Metals*, 1951, **79**, 379.
2. R. Osadchuk, W. P. Koster, and J. F. Kahles, *Metal Progress*, 1953, **64**, (4), 129.
3. P. Petrokowsky and P. Duwez, *Trans. Amer. Inst. Min. Met. Eng.*, 1951, **191**, 772.
4. A. D. McQuillan, *J. Inst. Metals*, 1951, **79**, 73.
5. M. K. McQuillan, *ibid.*, 1953-54, **82**, 433.
6. H. W. Worner, *ibid.*, 1952-53, **81**, 521.
7. A. D. McQuillan, *ibid.*, 1954-55, **83**, (5), 181.

1626 EQUILIBRIUM RELATIONS AT 460° C. IN ALUMINIUM-RICH ALLOYS CONTAINING 0-7% COPPER, 0-7% MAGNESIUM, AND 2.0% SILICON *

By H. J. AXON,† B.Met., D.Phil., MEMBER

SYNOPSIS

The equilibrium isothermal at 460° C. is given for quaternary alloys rich in aluminium and containing 0-7 wt.-% magnesium, 0-7 wt.-% copper, and constant (2.0 wt.-%) silicon. The results are related to previously published diagrams for alloys containing 1.2% silicon (*J. Inst. Metals*, 1952-53, **81**, 209) and 0.6% silicon (*ibid.*, 449), and the form of the aluminium-rich solid solution field at 460° C. is evaluated.

I.—INTRODUCTION

THE 460° C. isothermal sections have already been published^{1,2} for constant silicon contents of 0.6 and 1.2% with copper and magnesium both in the range 0-7%. The purpose of the present note is to present new information about the 2.0% silicon section, and to consider the reliability with which a solid model of the aluminium-rich corner of the quaternary isothermal model may be constructed. The experimental methods and system of nomenclature have already been described,¹ and, as before, the chemical analyses were conducted by Messrs. Johnson, Matthey and Co., Ltd., to whom the author's thanks are due.

II.—EXPERIMENTAL RESULTS

The general form of the quaternary isothermals for 0.6 and 1.2% silicon at 460° C. enables a rough estimate to be made of the positions of the phase fields in the 2.0% silicon section. Thus, a relatively limited number of specimens containing 2.0% silicon enable the section to be mapped out with a fair degree of accuracy.

Fig. 1 shows the phase fields which occur on annealing aluminium-rich alloys containing 2.0% silicon for 4 weeks at 460° C. In Fig. 1 the point X on the vertical axis is taken from the ternary aluminium-copper-silicon system and corresponds to the $(\alpha + \text{Si})/(\alpha + \text{Si} + \theta)$ phase boundary for alloys containing 2.0% silicon. Points Y and Z on the horizontal axis are taken from the ternary aluminium-magnesium-silicon system, and correspond respectively to the $(\alpha + \text{Si})/(\alpha + \text{Si} + \text{Mg}_2\text{Si})$ and the $(\alpha + \text{Si} + \text{Mg}_2\text{Si})/(\alpha + \text{Mg}_2\text{Si})$ phase boundaries for alloys containing 2.0% silicon. The points in Fig. 1 which correspond to analysed alloys are denoted by the letter A placed near the points. The probable limits of accuracy of this figure are : as regards temperature,

460° \pm 2° C., and as regards composition, silicon 2.0 \pm 0.03%, with 0.04% iron.

Comparison of Fig. 1 with the already published sections for 0.6 and 1.2% silicon shows that the general form of equilibrium at the aluminium-rich corner of the quaternary system is dominated by the two-phase $(\alpha + Q)$ field, by a number of four-phase fields which may be regarded as being disposed about the $(\alpha + Q)$ field, and by the $(\alpha + \text{Mg}_2\text{Si} + \theta + S)$ phase field, which may be regarded as an extension into the quaternary system of the $(\alpha + \theta + S)$ field of the ternary aluminium-copper-magnesium system. The $(\alpha + Q)$ phase field represents a quasi-binary relationship between the aluminium-rich α solid solution and the quaternary phase, Q, which has been designated $\text{Al}_3\text{Cu}_2\text{Mg}_3\text{Si}_6$ by Phragmén.³ In the three sections at 0.6, 1.2, and 2.0% silicon, it has been found possible to represent the experimental results for the $(\alpha + Q)$ field by an area of similar shape and dimensions which moves away from the aluminium-rich corner as the silicon content is increased. The three corners of the $(\alpha + Q)$ field come into contact with the corners of three separate fields of four-phase equilibrium. These four-phase fields contract in area as the silicon content is reduced, and since they must be bounded by ruled surfaces it seems permissible to extrapolate the existing data to lower silicon contents in order to find the compositions at which the four-phase fields close completely in the quaternary model. Using a linear extrapolation, this has been done for the three fields of four-phase equilibrium which are disposed about the $(\alpha + Q)$ field. Of these phase fields, the $(\alpha + \text{Mg}_2\text{Si} + \text{Si} + Q)$ field may be regarded as contracting to a point as the silicon content of the alloys is reduced, and, moreover, this point represents the composition at which the aluminium-rich corner of the $(\alpha + Q)$ field comes into equilibrium with the aluminium-rich α solid solution. This composition is represented by the point G in Fig. 2. It should, however, be remem-

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bered that no direct experimental evidence was obtained for the positions of the boundaries of the $(\alpha + \text{Mg}_2\text{Si} + \text{Si} + Q)$ field at 0.6% silicon, and in this section the field was drawn in a manner which seemed plausible in the light of knowledge then existing. Thus the point of disappearance of the $(\alpha +$

aluminium-rich α solid solution, and are denoted by points *B* and *C* in Fig. 2. It will be appreciated that the $(\alpha + \text{Si} + Q)$ and $(\alpha + \text{Mg}_2\text{Si} + Q)$ fields of the quaternary model have contracted to produce the lines *GB* and *GC* of Fig. 2. In making these extra-

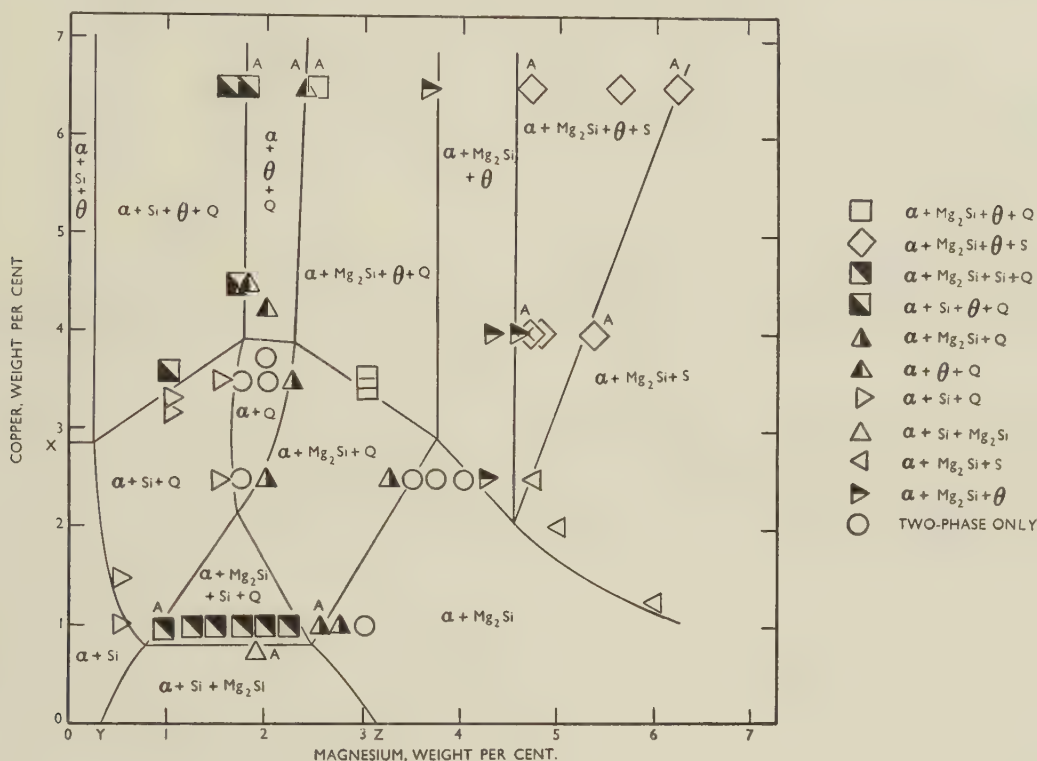


FIG. 1.—The 460° C. Isothermal for the System Aluminium-Copper-Magnesium-Silicon. All alloys in this figure contain 2.0 wt.-% silicon.

$\text{Mg}_2\text{Si} + \text{Si} + Q)$ field is obtained by the linear extrapolation of results from the 1.2 and 2.0% silicon sections *only*, and this extrapolation suggests that a more plausible form of the $(\alpha + \text{Mg}_2\text{Si} + \text{Si} + Q)$ triangle at 0.6% silicon would have its corners at (Cu 0.5, Mg 0.53%), (Cu 0.3, Mg 0.5%), (Cu 0.3, Mg 0.57%), instead of at the values (Cu 0.8, Mg 0.5%), (Cu 0.5, Mg 0.4%) which were previously chosen. It will be seen that whereas the alteration to the magnesium figure is very small, the copper contents are reduced appreciably, and the total result is to make the triangle in the 0.6% silicon section more nearly equilateral, at the same time reducing its area and moving it to lower copper and slightly higher magnesium values.

In a similar manner we may visualize the line separating the $(\alpha + \text{Si} + \theta + Q)$ and $(\alpha + \text{Si} + Q)$ fields and the line separating the $(\alpha + \text{Mg}_2\text{Si} + \theta + Q)$ and $(\alpha + \text{Mg}_2\text{Si} + Q)$ fields both decreasing to a point as the silicon content is reduced. These points would correspond, respectively, to the compositions at which the copper-rich and magnesium-rich corners of the $(\alpha + Q)$ region come into equilibrium with the

equilibrium were found to vary in a strictly linear manner with silicon content, and no adjustment is necessary when the three sections are fitted into the quaternary isothermal model.

The form of the $(\alpha + \text{Mg}_2\text{Si} + \theta + S)$ phase field is interesting in so far that, within the limits of the

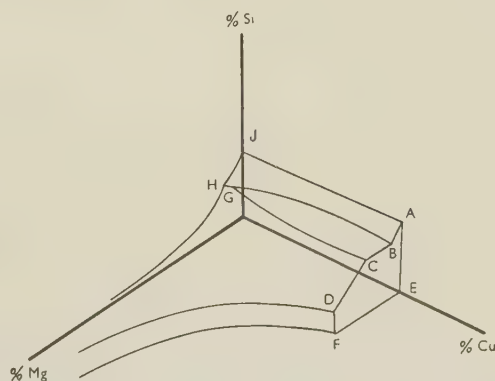


FIG. 2.—The Form of the Aluminium-Rich α -Solid-Solubility Region in the Aluminium-Copper-Magnesium-Silicon System at 460° C.

present investigation, it appears to have approximately the same dimensions in the three sections for 0.6, 1.2, and 2.0% silicon, and, moreover, to have in these sections approximately the same dimensions as the ($\alpha + \theta + S$) field of the ternary system on to which it must be grafted. If, however, the point at which the ($\alpha + \text{Mg}_2\text{Si} + \theta + S$) field comes into equilibrium with the ($\alpha + \text{Mg}_2\text{Si}$) field is considered in detail, it is found that a strictly linear relation exists between the compositions of these points for the three sections within the quaternary model, but that this linear relationship does not extend to the apex of the ($\alpha + \theta + S$) field in the ternary diagram. The ternary and quaternary phase fields may be grafted together if it is assumed that the three-phase ($\alpha + \theta + S$) field extends upwards into the quaternary model to the extent of about 0.15% silicon (point *D* of Fig. 2) without altering in width or position; at this value it is cut off by a plane parallel to the aluminium-magnesium-copper composition plane and thus separated from the ($\alpha + \text{Mg}_2\text{Si} + \theta + S$) field, the apex of which moves to higher magnesium and slightly lower copper values as the silicon content is increased.

Fig. 2 represents the limits of the region of α solid solubility at 460° C. and the probable compositions of the various points in this figure, as obtained from

the extrapolation of data within the quaternary model, are given in Table I.

TABLE I.—*Compositions at Points in Fig. 2.*

Point	Cu, %	Mg, %	Si, %
A	2.85	0.00	0.50
B	2.88	0.125	0.40
C	2.83	0.525	0.40
D	2.75	1.20	0.14
E	2.90	0.00	0.00
F	2.75	1.20	0.00
G	0.20	0.375	0.45
H	0.00	0.35	0.35
J	0.00	0.00	0.51

ACKNOWLEDGEMENTS

The author thanks Professor F. C. Thompson for research facilities and The Royal Society for a grant in aid.

REFERENCES

1. H. J. Axon, *J. Inst. Metals*, 1952-53, **81**, 209.
2. H. J. Axon, *ibid.*, 1952-53, **81**, 449.
3. G. Phragmén, *ibid.*, 1950, **77**, 489.

By R. W. CAHN,† Ph.D., A.Inst.P., MEMBER

SYNOPSIS

Molybdenum was found to twin by the same mechanism as iron, when single crystals were compressed by impact at the temperature of liquid oxygen. The crystals were also very malleable under these extreme conditions. Twinned crystals contained large cracks which were probably nucleated at junctions of two twin bands. The orientation of the twinned lattice was determined by the X-ray precession method, which has distinct advantages over the Laue method for this purpose.

I.—INTRODUCTION

THE body-centred cubic form of iron can be twinned by mechanical action. The twinning plane, which is also the interface between the two individuals constituting the twin, is $\{112\}$, and the twinning shear is parallel to $\langle 111 \rangle$. The fact, often disputed, that the bands visible in the microstructure of deformed iron are, indeed, in twin orientation to the original crystal, has been confirmed by examination of etch-pits¹ and by X-rays,² and the expected direction and magnitude of shear have been verified goniometrically by Paxton.³ The shear direction was also shown to be $\langle 111 \rangle$ by study of the intersection of pairs of twin bands.⁴

The purpose of the present experiments was to look for mechanical twins in molybdenum, which has the same structure as iron, and to apply complete crystallographic tests to establish firmly that they were twins. The only previous report of twin-like bands in molybdenum is due to Bechtold,⁵ who published a photomicrograph of "Neumann bands" in a polycrystalline specimen fractured at -196°C . These were not further examined. There is limited metallographic evidence of twinning in chromium hammered at room temperature,⁶ and in tungsten fractured at a range of temperatures.⁷ β -Brass will not twin under any conditions.⁸ These substances all have the same structure as iron and molybdenum.

II.—EXPERIMENTAL

1. PROCEDURE

Single crystals were used, to facilitate crystallographic tests, and because the absence of grain boundaries generally favours twinning at the expense of slip. Since Bechtold's work suggested that it would be necessary to strain at a low temperature, and the tensile ductility of molybdenum below room temperature is small, it was decided to test single crystals in compression. A supply of small crystals was available (Fig. 3, Plate LXXII). These were the product of accidentally overheating and locally evaporating a

molybdenum rod while this was being heated *in vacuo* by the passage of an electric current. The metal vapour condensed on the cooler parts of the rod in the form of dodecahedra, up to about 0.7 mm. across the flats, and connected to the parent rod by a slender

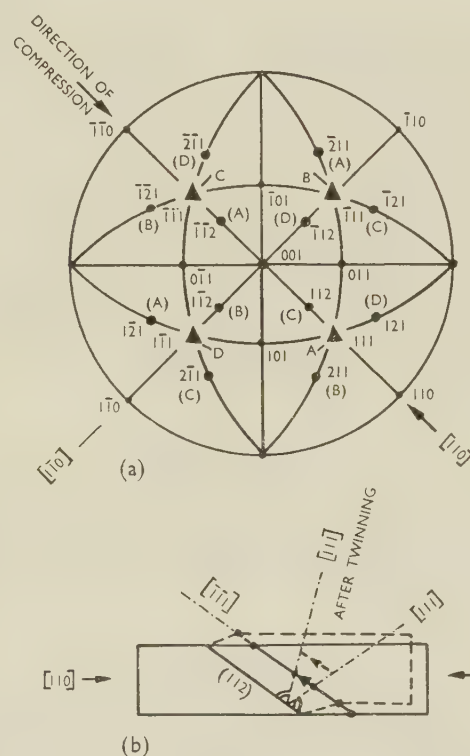


FIG. 1 (a).—Twinning Planes and Shear Directions in a Molybdenum Crystal.

FIG. 1 (b).—Contraction of Specimen by Twinning on $\{112\}$.

stem.⁹ One crystal was measured on a two-circle optical goniometer, and the interfacial angles were found to be close to 90° or 60° , confirming that the faces were parallel to $\{110\}$ planes.

On the hypothesis that molybdenum does twin in the same way as iron, Fig. 1 (a) has been drawn to show

sity, Baltimore, Maryland, U.S.A., at the time of these experiments.

* Manuscript received 15 February 1955.

† Lecturer in Physical Metallurgy, University of Birmingham, England. Visiting Lecturer at Johns Hopkins Univer-

TABLE I.—*Angle of Tilt θ of a Twin Band on a $(10\bar{1})$ Face.*

(iii) A subsidiary crack sometimes extends from the tip of a terminating twin band or from the junction of two twin bands. In Fig. 10 (Plate LXXII) band *A* appears to have been formed first, then band *B* impinged upon *A*. A great tensile stress develops as a consequence of the shear discontinuity at the junction (the shears are indicated in the figure). A crack

spreads, first tearing the twin interface, then veering along the cleavage plane (001).

III.—SUMMARY AND DISCUSSION

The present investigation has shown that: (1) twin bands in molybdenum form only during impact at low temperature; (2) they form only on those planes which allow the specimen as a whole to contract under the applied compressive force; (3) the bands are parallel to {112}; (4) the direction and magnitude of shear are consistent with the twinning mechanism as established for iron, i.e. a $\langle 111 \rangle$ shear direction and a shear of 0.707; and (5) twinning is associated with the formation and spread of cracks.

The malleability of the crystals is very large even under impact in liquid oxygen. The very small crystals had the highest malleability, but did not usually twin or fracture. It is conceivable that these small crystals became momentarily heated to a high temperature by the absorbed kinetic energy of the tup, which would account for their great malleability. But the larger crystals, at least, were being deformed much below the conventional temperature of transition from ductile to brittle behaviour, yet they suffered reductions in height of up to 50%. This indicates that the transition is a characteristic only of polycrystals. This idea is consistent with the recently reported observation¹¹ that a large grain in polycrystalline molybdenum, the transition temperature of which had been raised by contamination with oxygen, was itself very ductile, though it snapped away easily from a neighbouring grain. Again, Steijn and Brick¹² have shown, and Biggs¹³ has confirmed, that single crystals of iron, provided their orientation is favourable, have good tensile ductility at temperatures at which the same material in polycrystalline form would be brittle.

It would be instructive to carry out systematic experiments on the temperature-dependence of the ductility of single crystals of body-centred cubic metals, tested in tension or flexure, and also on the transition to brittle behaviour of polycrystals tested in compression.

The main longitudinal cracks observed in the present experiments were probably nucleated by impinging pairs of twin bands, as sketched in Fig. 14. The two twin bands and the crack all intersect along the common direction $[1\bar{1}0]$. The crack of Fig. 10 shows that

this mechanism is feasible; moreover, the side-tracking of a spreading crack along twin interfaces, as illustrated in Fig. 8, proves that some, at least, of the twin bands precede the crack. Good metallographic evidence of the nucleation of cracks by twin pairs in zinc crystals has recently been obtained by Bell.¹⁴ On the other hand, there is a possibility that some of the twin bands are nucleated at the tip of the advancing crack, where the stress concentration is great; this has in fact been observed,¹⁵ again in zinc crystals,

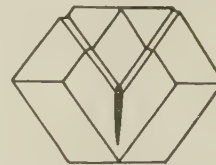


FIG. 14.—Probable Genesis of Large Cracks.

although these were of a different orientation from Bell's. The only way of determining the sequence of events in the present instance for certain is to follow the process by high-speed cinematography.

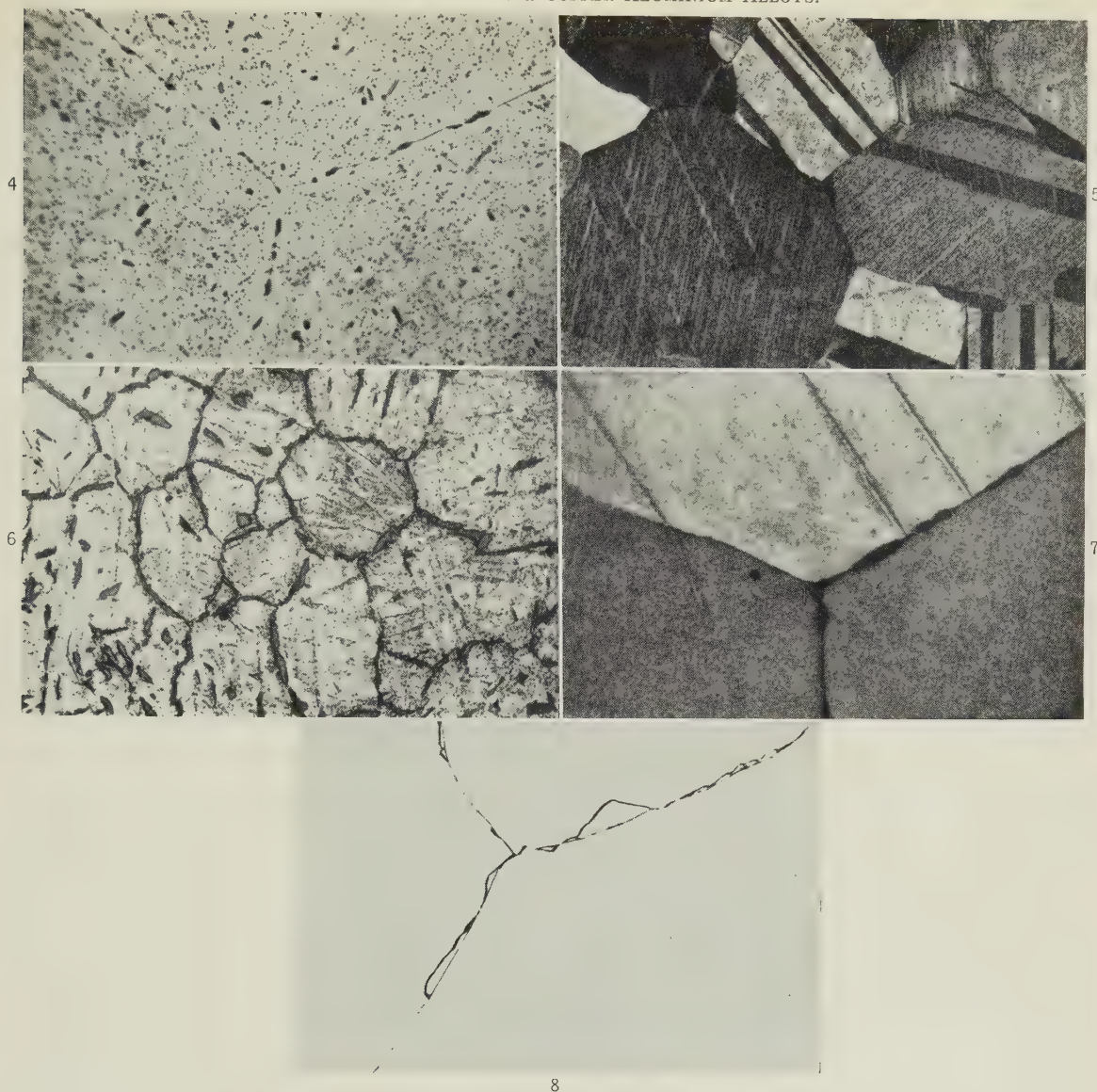
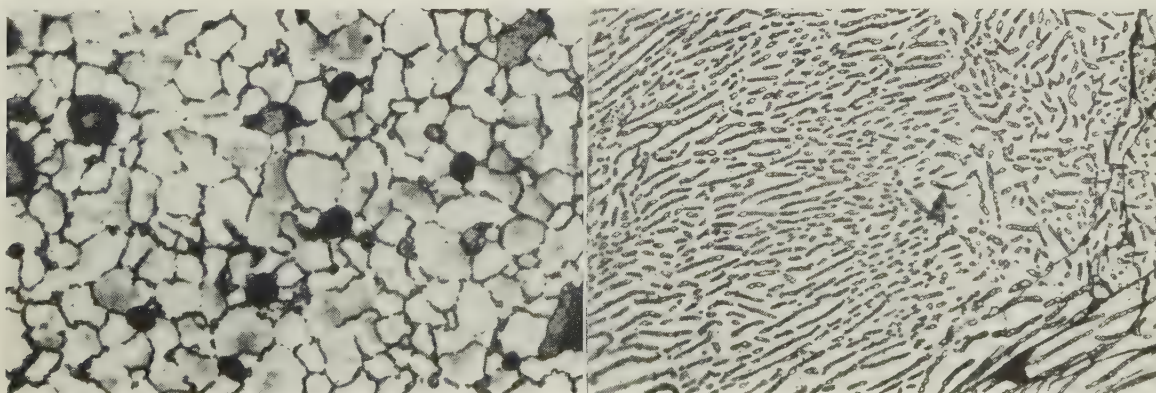
The verification that molybdenum twins in the same way as iron makes it highly probable that the observed bands in deformed tungsten and chromium are also twins of the same type. A group of the body-centred metals is then seen to behave in a uniform manner, just as do the close-packed hexagonal metals. The failure to create mechanical twins in β -brass⁸ can be explained in terms of the superlattice which is always present at temperatures when twinning might otherwise be expected. Laves¹⁶ has shown that the superlattice would have to be destroyed before twinning can proceed, and the resistance to such destruction is too great to be overcome.

ACKNOWLEDGEMENTS

Thanks are due to the authorities of the Johns Hopkins University, Baltimore, for the opportunity to carry out this research during the tenure of a Visiting Lectureship. The United States Office of Naval Research gave financial support. Professor J. D. H. Donnay and Dr. G. Donnay kindly made available their X-ray precession camera and advised on its correct use. Professor R. Pond's help and advice are also gratefully acknowledged, as are Dr. P. L. Pratt's comments on the MS.

REFERENCES

1. K. Harnecker and E. Rassow, *Z. Metallkunde*, 1924, **16**, 312.
2. A. Kelly, *Proc. Phys. Soc.*, 1953, [A], **66**, 403.
3. H. W. Paxton, *Acta Met.*, 1953, **1**, 141.
4. S. W. J. Smith, A. A. Dee, and J. Young, *Proc. Roy. Soc.*, 1928, [A], **121**, 477.
5. J. H. Bechtold, *Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197**, 1469.
6. W. E. Carrington, *J. Inst. Metals*, 1953-54, **82**, 170.
7. J. H. Bechtold and P. G. Shewmon, *Trans. Amer. Soc. Metals*, 1954, **46**, 397.
8. C. S. Barrett, *Trans. Amer. Inst. Min. Met. Eng.*, 1954, **200**, 1003.
9. R. Maddin and N. K. Chen, *Iron Age*, 1952, **170**, (17), 108.
10. M. J. Buerger, *Amer. Soc. X-Ray and Electron Diffraction Monograph No. 1*, (1944).
11. R. E. Maringer and A. D. Schwoppe, *Trans. Amer. Inst. Min. Met. Eng.*, 1954, **200**, 365.
12. R. P. Steijn and R. M. Brick, *Trans. Amer. Soc. Metals*, 1954, **46**, 1406.
13. W. D. Biggs, private communication.
14. R. L. Bell, private communication.
15. A. Deruytère and G. B. Greenough, *Phil. Mag.*, 1954, [vii], **45**, 624.
16. F. Laves, *Naturwiss.*, 1952, **39**, 546.

PHOTOMICROGRAPHS OF α COPPER-ALUMINIUM ALLOYS.FIG. 4.—1.52% Fe, 6.16% Al Alloy, Slowly Cooled from 1000° C. $\times 250$.FIG. 5.—1.09% Co, 0.96% Fe, 6.71% Al Alloy Aged at 600° C. $\times 250$.FIG. 6.—1.72% Co, 4.97% Ni, 6.88% Al Alloy Slowly Cooled from 1000° C. $\times 100$.FIG. 7.—1.54% Co, 6.85% Al Alloy, Aged at 400° C. Creep-rupture at 300° C., 4 tons/in.². Showing cavitation. $\times 750$.FIG. 8.—1.52% Fe, 6.16% Al Alloy, Solution-Treated. Creep at 4 tons/in.² for 300 hr. Grain-boundary movement. $\times 250$.PHOTOMICROGRAPHS OF Cr_3C_2 -TiC ALLOYS.FIG. 3.—60% TiC, 40% Cr_3C_2 . Rapidly cooled from 1615° C. Electrolytically etched with oxalic acid. $\times 750$.FIG. 4.—4% TiC, 96% Cr_3C_2 . Slowly cooled from 1770° C. Electrolytically etched with oxalic acid. $\times 1000$.

MICROSTRUCTURES OF TITANIUM-GERMANIUM ALLOYS.

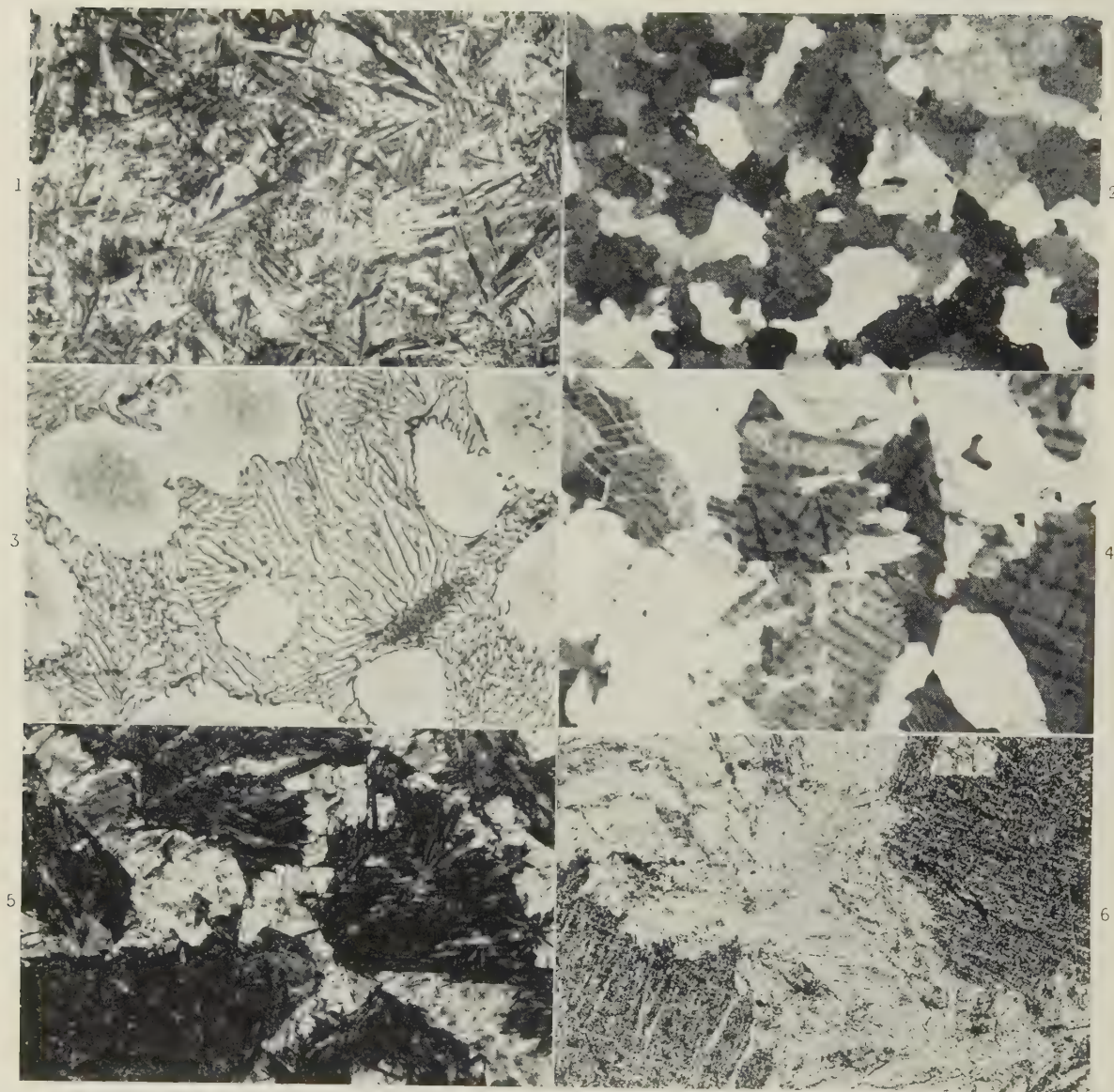


FIG. 1.—4 At.-% Germanium Alloy, Heated at 900° C. Transformed $\beta + \text{Ti}_3\text{Ge}_3$. $\times 100$.

FIG. 2.—4 At.-% Germanium Alloy, Heated at 894° C. Equiaxed $\alpha + \text{Ti}_3\text{Ge}_3$. $\times 100$.

FIG. 3.—10.8 At.-% Germanium Alloy As Cast. Primary β (transformed) + $\beta\text{-Ti}_3\text{Ge}_3$ eutectic. $\times 1000$.

FIG. 4.—6 At.-% Germanium Alloy, As Cast. Serrated α . $\times 56$.

FIG. 5.—Same Alloy as Fig. 4 Heated for 3 Days at 750° C. $\alpha + \text{Ti}_3\text{Ge}_3$. $\times 56$.

FIG. 6.—6 At.-% Germanium Alloy Cooled from 1325° C. and Reheated for 3 Days at 800° C. $\alpha + \text{Ti}_3\text{Ge}_3$. $\times 56$.

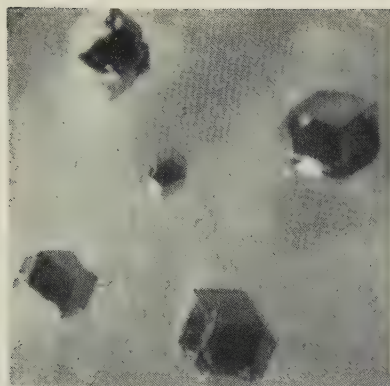


FIG. 3.—Undeformed Molybdenum Crystals. $\times 15$.



FIG. 4.—Twinned Crystal, Viewed along Compression Direction $[110]$. $\times 45$.



FIG. 5.—Another Twinned Crystal, Viewed Along $[110]$, at Right Angles to Compression Direction. $\times 45$.

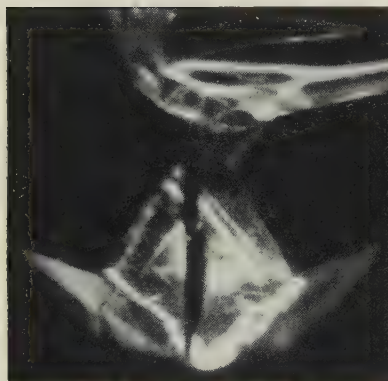


FIG. 6.—As Fig. 5, but Opposite Side of Crystal. $\times 45$.

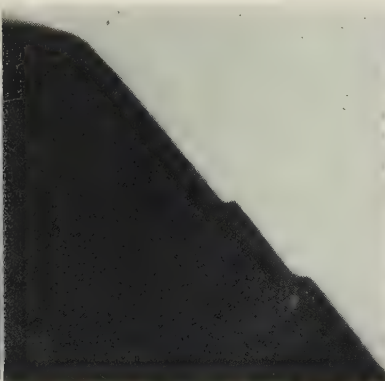


FIG. 7.—Profile of Two Twin Bands at the Edge Between the (011) and (101) Faces. $\times 450$.

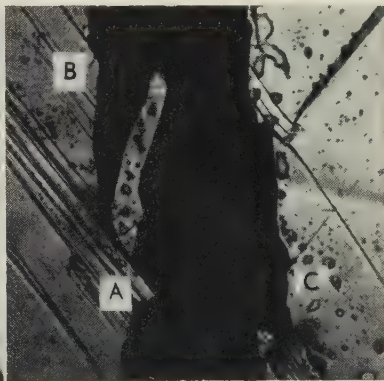


FIG. 8.—Side-Tracking of Walls of Crack Along Existing Twin Bands on (110) Face. $\times 450$.

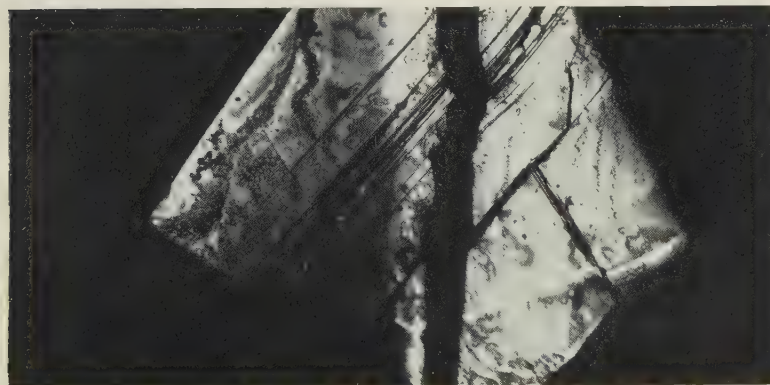


FIG. 9.— (110) Face of Twinned Crystal with a Large Crack. $\times 150$.

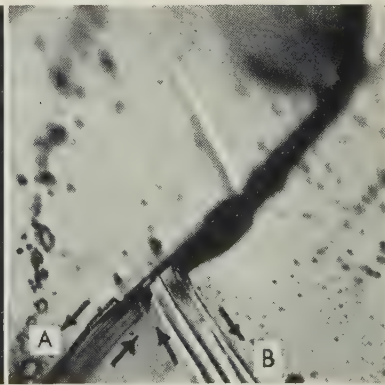


FIG. 10.—Crack Spreading from Junction of Two Twin Bands (detail of Fig. 9). $\times 750$.



FIG. 11.—Portion of Precession Photograph of Undeformed Crystal, Showing Reciprocal Lattice Plane $\perp [1\bar{1}0]$. Filtered MoK radiation, 45 kV., 60 m.amp.-hr.



FIG. 12.—Portion of Precession Photograph of Deformed Molybdenum Crystal, Showing Reciprocal Lattice Plane $\perp [1\bar{1}0]$. Filtered MoK radiation, 45 kV., 900 m.amp.-hr. Spots due to twinned lattices are marked by arrows.

By A. G. KNAPTON,† B.Sc., Ph.D., JUNIOR MEMBER

SYNOPSIS

The liquidus and solidus in the uranium-titanium system show a smooth increase from the melting point of uranium to that of titanium. A continuous series of solid solutions is formed between the γ -modification of uranium and the β -modification of titanium.

The addition of titanium lowers the $\beta \rightarrow \gamma$ transformation from 771° C. in pure uranium to a eutectoid with the intermediate ϵ (U₂Ti) phase at 723° C., 4 at.-% titanium. β -Uranium dissolves about 1½ at.-% titanium at the eutectoid temperature.

An hexagonal phase, ϵ , having the C32 structure, separates at 898° C. from the γ solid solution.

A eutectoid is formed between ϵ and α -titanium at 655° C., 83 at.-% titanium. The solubility of uranium in α -titanium at the eutectoid temperature is about 0.8 at.-%, and the solubility of titanium in α -uranium is <1 at.-%.

I.—INTRODUCTION

An investigation of the uranium-titanium system has been carried out by metallographic, X-ray, and dilatometric methods. During the course of the work several publications¹⁻³ on uranium-titanium alloys have appeared in America.

Buzzard and his co-workers¹ examined alloys containing up to 30 at.-% titanium. This limit was imposed by the H.F. melting method used for preparing the alloys. Their diagram shows a liquidus rising from the melting point of uranium to a peritectic at 1180° C., 8 at.-% titanium, and then rising steeply to 1950° C., 30 at.-% titanium. The γ -uranium solid solution was followed by a δ phase, which decomposed eutectoidally at 830° C. In this diagram, the δ phase appears to have a high melting point.

Udy and Boulger² have reported an investigation of the whole uranium-titanium system. High-purity materials were used, and arc-melting in helium, followed by hot working, was employed for preparing the alloys. These workers have found complete solid solubility above 1150° C. between the γ -uranium and β -titanium. No discontinuities were found in the liquidus curve, which rises smoothly from the melting temperature of uranium to that of titanium. The diagram shows that the γ solid solution decomposes at 1150° C. and 33 at.-% titanium into an hexagonal phase, U₂Ti, of parameters $a_0 = 4.817$, $c_0 = 2.844$ Å. This phase forms eutectoids at 620° C., 72 at.-% titanium with α -titanium, and at 718° C., 5 at.-% titanium with β -uranium. The compound is reported to exist over a wide composition range with a maximum of *c.* 28–40 at.-% at 720° C.

A subsequent publication by Udy and Boulger³ gives a revised diagram, in which the U₂Ti phase is stable up to about 890° C., instead of 1150° C. as previously reported.

II.—EXPERIMENTAL PROCEDURE

1. MATERIALS USED

The uranium used was provided by the Ministry of Supply. The bulk of the work was carried out on uranium bar material, which contained numerous coarse oxide particles after arc-melting. The presence of this oxide gave rise to difficulties in the examination of high-uranium alloys. Towards the end of the investigation, a small quantity of coarse powder uranium became available, and this, after arc-melting, proved to be considerably cleaner than the bar. The uranium-rich end of the system was re-examined, using this purer material.

The titanium was an I.C.I. iodide material of hardness 100–120 V.P.N. A typical analysis of this metal, as given by the suppliers, is:

Fe	Mg	Si	C	N
0.1%	0.02–0.03%	0.01%	0.1%	0.02%

2. ALLOYING

The alloys were prepared by arc-melting on a copper hearth in an atmosphere of purified argon. To ensure homogeneity and complete melting, the alloy buttons were limited in size to 10–25 g., and each alloy was melted four times. Between each melting operation, the buttons were turned over.

Before being used for alloying, all uranium was arc-melted to convert it into a more suitable form for further use or to remove gases or inclusions which frequently caused spitting losses on first melting the metal. Before melting, the uranium was pickled in a 1:1 nitric-acetic acid mixture to remove the superficial oxide film, washed in water and alcohol, and dried in a stream of cool air. The metal was immediately loaded into the arc furnace, and the chamber was

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evacuated as rapidly as possible to prevent further oxidation.

The weight loss on alloying was usually quite small (0.5–1.0%). Alloys which showed greater weight losses than this were not used for further examination, and the melts were repeated.

Ingots $1\frac{1}{4}$ in. long by $\frac{1}{4}$ in. dia., required for dilatometric examination or cold-rolling experiments, were formed in a shaped hearth in the arc furnace from material already alloyed.

3. ANNEALING TREATMENTS

Microscopic heterogeneity in the specimens after arc-melting was removed by annealing at 930°–950° C. for 1 month. Annealing was carried out in evacuated silica capsules, alumina collars being used to separate the specimens and to prevent them from touching the walls of the capsule. Before sealing, each capsule was evacuated to a pressure of $<10^{-5}$ mm. mercury. Absorbed gases were removed by baking the capsule and contents at 400°–500° C. during pumping. Some superficial oxidation of the specimens occurred during the homogenizing treatment, probably mainly as a result of the slight permeability of silica to air at elevated temperatures. A considerable measure of protection was obtained, however, by including a quantity of scrap uranium and titanium turnings of large surface area in the capsule with the specimens.

High-titanium alloys (75–100 at.-% titanium) were cold rolled to about 50% reduction before homogenizing and packed in titanium turnings in the silica capsules.

For annealing below 900° C., alloy sections were wrapped in 0.001-in. molybdenum foil and heated in evacuated and baked silica capsules. No significant pick-up of molybdenum could be detected in alloys annealed in this manner. After a few preliminary experiments, heat-treatment times for lump specimens for metallographic examination were standardized as follows:

850°	800°	750°	700°	650°	600° C.
7	10	14	21	28	42 days

All heat-treatments below 1000° C. were carried out in tubular resistance furnaces, which could be controlled to $\pm 1^\circ$ C. for long periods by using Sunvic-RT2 platinum-resistance thermometer controllers.

All specimens were quenched by breaking the silica capsules under water immediately on removal from the furnace. For solidus determinations up to 1500° C., annealing was carried out in a vertical platinum-wound tube furnace in an atmosphere of purified argon. The specimens were suspended in a tungsten-wire cage, and quenched into cooled oil through a cellophane window at the lower end of the furnace. The specimen temperature was measured with a platinum/platinum-rhodium thermocouple in close proximity to the specimen in the furnace. The treatment resulted in some contamination of the surface of the specimen, and only the central regions of the

specimens were examined metallographically. Separate specimens were used for each solidus determination, so that no cumulative contamination could occur.

4. X-RAY METHODS

Copper K_α radiation from a Raymax rotating-anode set was used in the X-ray investigations. Exposure times of 20 min.–1 hr. were necessary at an output of 85 m.amp., at 50 kV. Powder and glancing-angle methods were used for X-ray examinations at room temperature. Glancing-angle photographs were usually taken on Bakelite-mounted metallographic specimens, which enabled X-ray and metallographic results to be compared directly.

Powder specimens were prepared from the alloy sections containing 20–65 at.-% titanium by grinding in a tungsten-carbide mortar. Alloys of other compositions were not sufficiently brittle for this to be done, and had to be powdered by filing. For low-temperature annealing, to relieve strains introduced during powdering, the specimens were sealed in small evacuated silica capsules, which were baked at 400°–500° C. before sealing. For higher-temperature treatments, the powders were first placed in alumina sheaths, and sealed in silica as before.

5. HIGH-TEMPERATURE X-RAY METHODS

A Unicam high-temperature camera modified in a manner similar to that described by Berry and his co-workers⁴ was used for high-temperature X-ray work. Specimens were prepared from alloy lump sections which had been previously annealed and quenched from the temperature at which it was intended to take the X-ray photograph. The filings were sealed in 0.7-mm.-dia. silica quills, under a vacuum of 10^{-5} mm. after baking at 400°–500° C. In the camera, the specimens were heated as rapidly as possible, and given a short anneal of $\frac{1}{2}$ –1 hr. before exposure. In general, exposure times of 3–5 hr. were required at 50 kV. and 85 m.amp.

6. AUTORADIOGRAPHY

A uranium rod was forced into a hole in a section of iodide titanium and the composite specimen annealed for 4 months at 650° C. Diffusion at the interface leads to the formation, in each metal, of a zone which for some distance is of constant composition corresponding to a saturated solution of the other metal in it at the temperature of the experiment. Since the solubility of uranium in α -titanium may be measured by α track counts, a plot of the α track count against distance from the interface yields a constant value over the saturated zone.

An exposure time of 7 days was given on an Ilford Nuclear Research plate, Emulsion Type E1. The track counts were made on photomicrographs of the plate taken at a magnification of 600 \times , using a Vickers projection microscope.

7. METALLOGRAPHIC EXAMINATION

Metallographic specimens were polished on "Selvyt" cloth impregnated with 0-2 μ diamond dust in white spirit.

For alloys containing up to 75 at.-% titanium, an etching reagent of 50% nitric acid and 50% glacial acetic acid was used. High-titanium alloys were satisfactorily etched with an aqueous solution of 1% hydrofluoric and 3% nitric acid.

8. DILATOMETRY

Dilatometric examination of the alloys was carried out in a silica dilatometer, based on a design by Bangham and Franklin.⁵ An optical-lever system gave a magnification of about 4×10^3 . The dilatometer was used in a continuously evacuated furnace tube at a pressure of $<10^{-5}$ mm. mercury. A heating or cooling rate of about 1° C./min. was employed in the dilatometric experiments.

III.—THE CONSTITUTIONAL DIAGRAM

The proposed uranium-titanium equilibrium diagram is given in Fig. 1. The symbol γ is used to

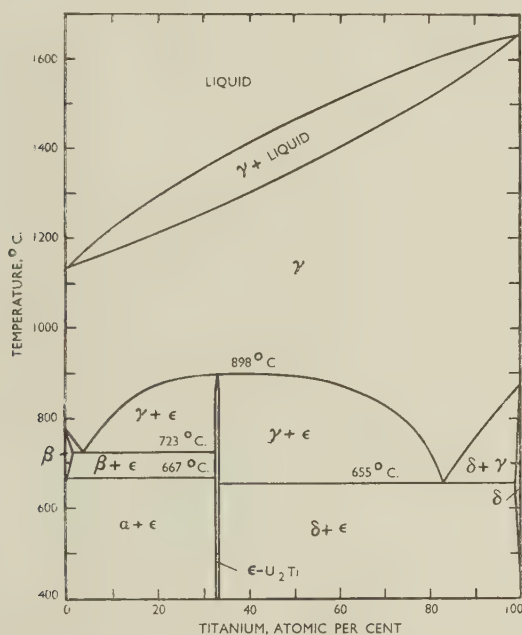


FIG. 1.—The Uranium-Titanium System.

designate the body-centred cubic solid solution between γ -uranium and β -titanium, and δ to denote the hexagonal close-packed α -titanium phase. The intermediate compound U_2Ti is denoted by ϵ . The experimental points on which the diagram is based are shown in Figs. 2 and 4. It will be noted in Fig. 2 that certain features of the diagram, such as the composition of the compound, appear to be shifted through about 2 at.-% towards the titanium end. The reasons for this

are explained later. In Fig. 1 this shift has been compensated for, but there remains a measure of uncertainty of perhaps 1-2 at.-% in the position of the boundaries. The points given in Figs. 2 and 4 are based on intended compositions in most cases. Twenty-five alloys have been analysed chemically for uranium and titanium, and the compositions of these alloys all fell within 1.1 at.-% of the intended composition. The use of intended compositions for such alloys appears to be justified, therefore.

1. LIQUIDUS AND SOLIDUS

The liquidus falls smoothly from the melting point of titanium to that of uranium. Optical-pyrometer determinations were successful on the solid/liquid junction of the alloy beads down to about 50 at.-% titanium.⁶ At lower titanium contents, a "skin" appeared to form over the bead and obscured the junction. The figures showed no trend towards a high-melting-point U_2Ti compound, as reported by some earlier workers.

The solidus temperatures for alloys in the composition range 0-70 at.-% titanium were bracketed by quenching from different temperatures. No discontinuities in the region of the composition of the compound were detected in the solidus results.

2. THE γ REGION

The γ modification of uranium and the β modification of titanium form a continuous series of body-centred cubic solid solutions. No direct evidence is available for the existence of γ in the whole of this region, but no structures have been observed in alloys quenched from above 900° C. that could be interpreted as having been quenched from a two-phase region.

X-ray investigations by the powder and glancing-angle techniques show that it is possible to retain γ on quenching over only a narrow composition range of 70-85 at.-% titanium. The lattice parameters of the body-centred solid solution from 70 to 90 at.-% titanium have been measured. The parameter value of the 90 at.-% titanium alloy has been measured on a partially transformed specimen. Taking the room-temperature parameter values of Tucker⁷ and of Wilson and Rundle⁸ for γ -uranium as 3.47 Å. and that of Levinger⁹ for β -titanium as 3.282 Å., it is shown in Fig. 3 that a linear relationship exists between the measured parameters and the atomic composition, with no marked deviation from Vegard's law.

The presence of γ at 750° C. in a 10 at.-% titanium alloy has been confirmed by high-temperature X-ray photography. Attempts to show the existence of γ in the field above the compound were not successful, a UO_2 pattern only being obtained in the high-temperature X-ray camera at 920° C.

Rapid quenching from 950° C. into iced brine, using small rod specimens at the composition of the compound (30-35 at.-% titanium), was not successful in

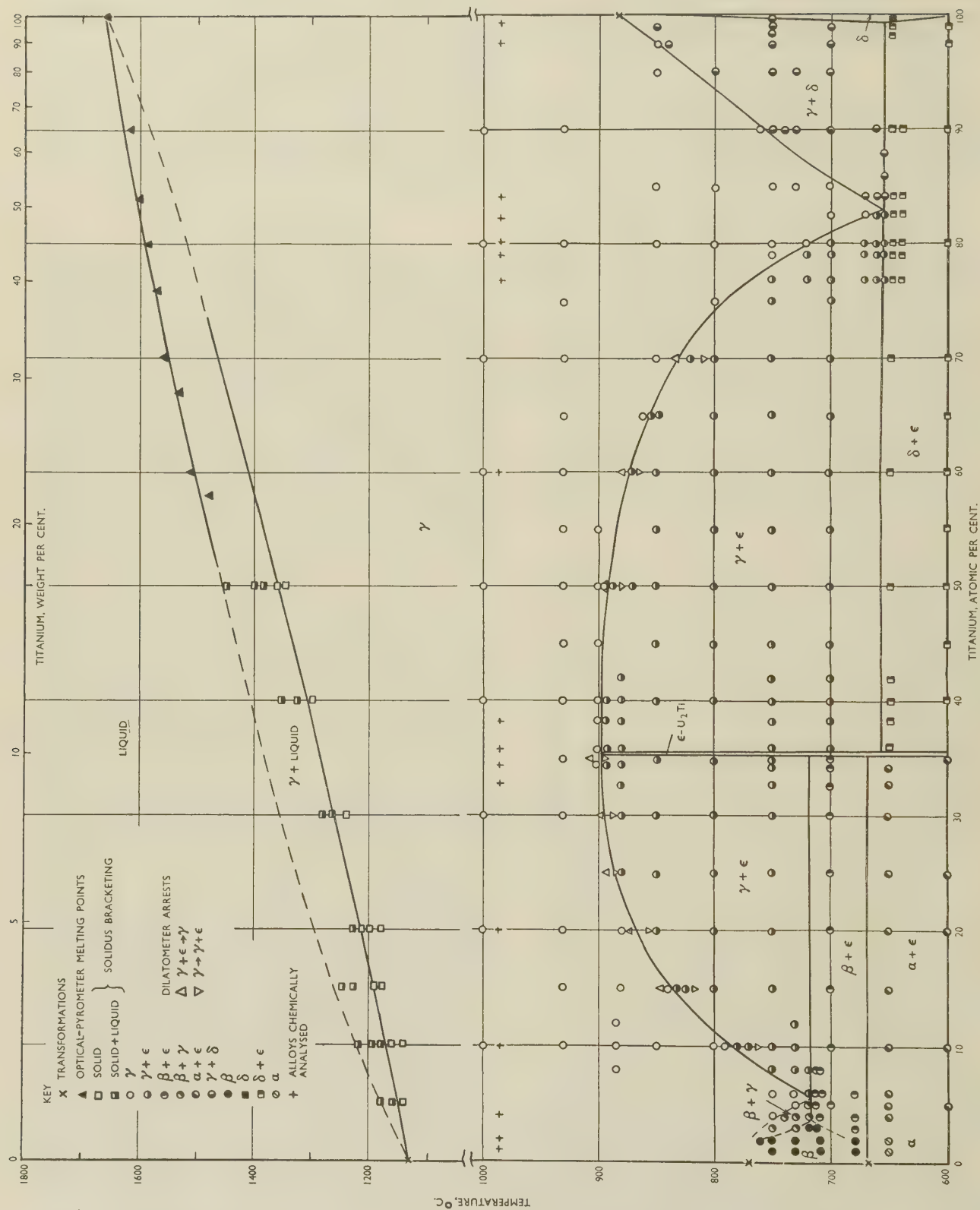


Fig. 2.—Experimental Points in the Uranium-Titanium System.

retaining the γ phase. A glancing-angle photograph on a fractured section of the rod taken immediately after quenching showed only the presence of ϵ .

The metallographic structures observed in specimens quenched from the γ field depend on the manner

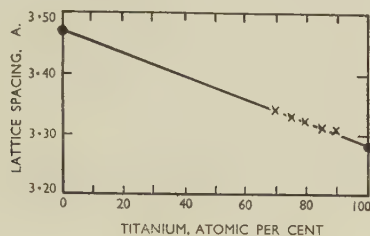


Fig. 3.—Lattice Parameters of γ -Phase Uranium-Titanium Alloys.

in which the transformation to the room-temperature-stable phase has taken place. In high-uranium alloys containing less than about 10 at.-% titanium, the γ solid solution decomposes to give the typical martensitic-type α -uranium structure.

An example of the "banded" structure reported by Buzzard, Liss, and Fickle,¹ and misinterpreted by these authors as belonging to a two-phase region, has been observed in one 10 at.-% titanium alloy specimen after homogenizing and quenching from the γ field (Fig. 5, Plate LXXIV). Subsequent alloys of the same composition, treated in the same manner, did not show this structure, and it is considered that the structure is not typical of uranium-titanium alloys, but may be associated with some unknown contaminant, although no contaminating elements were detected spectroscopically in the alloy showing the banded structure. Buzzard and his co-workers prepared uranium-titanium alloys by H.F. induction melting in beryllia crucibles in an atmosphere of argon, and the likelihood of contamination would be greater than for arc-melted alloys.

From its nature, the banded structure would appear to have been formed in a similar manner to the structures observed in copper-manganese,¹⁰ indium-thallium,¹¹ and vanadium-oxygen¹² alloys. It has been suggested that the structure is formed by a double shearing mechanism on specific planes, neighbouring bands representing regions sheared in opposite directions, and this type of mechanism is possibly operating during the transformation of the γ solid solution on quenching.

Alloys containing 15–65 at.-% titanium show fine unresolved transformation structures on being quenched from the γ region, and are all sufficiently brittle to be crushed with moderate ease. Glancing-angle X-ray photographs indicate that α -uranium is the principal phase present in alloys with 0–20 at.-% titanium quenched from the γ region. From 20 to 65 at.-% titanium, the predominant phase is ϵ .

Over a small range of titanium contents (70–85 at.-% titanium), the γ phase can be retained on quenching. At higher titanium contents, partial or complete transformation to the α -modification of

titanium takes place. A partially transformed 90 at.-% titanium specimen is shown in Fig. 6 (Plate LXXIV), dark-etching α -titanium needles being present in a matrix of untransformed γ .

3. THE $\beta + \gamma$ REGION

The solubility of titanium in β -uranium and the extent of the ($\beta + \gamma$) two-phase field were determined metallographically on water-quenched alloys. Alloy sections, after homogenizing at 930°–950° C., were annealed at several temperatures below the $\beta \rightarrow \gamma$ transformation temperature of uranium. On quenching, both the β and γ phases decompose into α , but the difference in titanium contents of the two phases enables them to be readily distinguished on etching.

The results from metallographic examination of quenched alloys made from uranium bar are shown in Fig. 4 (a). Alloys containing more than 3 at.-% titanium were obtainable with two-phase ($\beta + \gamma$) structures, a typical example of which is shown in Fig. 7 (Plate LXXIV) for a 4 at.-% titanium alloy. The decomposed β solid solution has etched dark in a

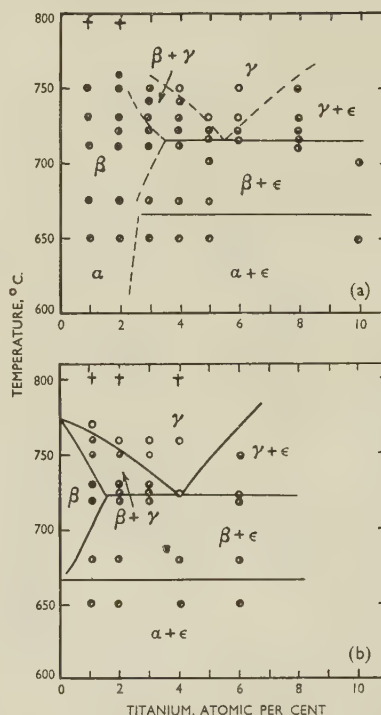


Fig. 4.—Results of Metallographic Examination of High-Uranium Alloys, Using (a) Bar Uranium and (b) Powder Uranium.

matrix of lighter-etching decomposed γ . The white, rounded particles are oxide inclusions, which were frequently found in arc-melted alloys made from uranium bar. Alloys containing 1 and 2 at.-% titanium could not be obtained in a two-phase state, suggesting that these additions of titanium were being lost and were not entering the γ solid solution.

Similar anomalous behaviour of alloys containing 1 and 2 at.-% titanium was noted in the dilatometric

investigation. In an arc-melted uranium bar specimen, the $\beta \rightarrow \gamma$ transformation occurred at 773° C. on heating and at 757° C. on cooling. The addition of 1 or 2 at.-% titanium to this material produced no significant change in the transformation, as shown in the dilatometer results collected in Table I. Alloys of higher titanium contents show that the $\beta \rightarrow \gamma$ transformation temperature is depressed to a eutectoid at about 5½ at.-% titanium and about 716° C. The temperatures reported for the $\beta \rightarrow \gamma$ transformation in Table I are for the beginning of the $\beta \rightarrow \gamma$ change on heating and for the beginning of the $\gamma \rightarrow \beta$ change on cooling.

A re-examination of alloys in this region of the diagram has been made, using arc-melted uranium powder as raw material. After melting, the metal was not completely free from oxide particles, but was considerably cleaner than the uranium bar. Alloys containing 1, 2, 3, 4, and 6 at.-% titanium were prepared from this material, and homogenized as before. They were then heated for 14 days at various temperatures, water-quenched, and examined metallographically. All alloys were found to behave much as would be expected for this part of the diagram, and the collected results are given in Fig. 4 (b).

TABLE I.—Transformation Temperatures as Indicated by Dilatometer Changes.

Titanium, at.-%	Temperature, °C.					
	$\alpha \rightarrow \beta$	$\beta \rightarrow \alpha$	$\beta \rightarrow \gamma$	$\gamma \rightarrow \beta$	$\gamma + \epsilon \rightarrow \gamma$	$\gamma \rightarrow \gamma + \epsilon$
(a) Alloys Made from Uranium Bar						
0	667	637	773	757
1	671	649	777	764
2	671	646	774	764
3	666	637	742	733
4	669	647	730	715
5	671	642	727	706
10	669	650	722	687	Not detected	750
15	668	641	722	688	841	817
20	674	643	724	691	877	853
25	669	642	722	691	893	881
30	672	640	723	689	894	887
35	905	895
50	891	878
60	883	864
70	833	809
(b) Alloys Made from Uranium Powder						
1	670	645	769	760
2	668	640	732	726
3	671	649	726	714

Dilatometric examination showed a depression in the $\beta \rightarrow \gamma$ transformation from that of pure uranium in alloys containing 1, 2, and 3 at.-% titanium. The observed temperatures are listed in Table I. From a comparison of the results on "bar" and "powder" specimens, it may be seen that alloys from the former metal behave in a similar manner to alloys with a titanium content about 1½ at.-% less made from the powder material. Chemical analyses of these speci-

mens indicated that alloys from both sources and of the same nominal compositions had nearly the same titanium contents. The difference in behaviour of the alloys is hence probably accounted for by some 1½ at.-% titanium reacting with some impurity or impurities in the bar uranium to form a stable compound, and not being available for forming the solid-solution γ phase. An impurity content of the order of 0.1 wt.-% carbon, nitrogen, and oxygen would be required in the uranium bar to give the effect observed if TiC, TiN, or TiO was the compound formed.

The chief conclusions from these investigations on the high-uranium region of the diagram are:

(a) The $\gamma \rightarrow \beta$ eutectoid occurs at about 4.0 at.-% titanium, 723° \pm 3° C.

(b) Solubility of titanium in β -uranium at the eutectoid temperature is about 1½ at.-%.

No attempts were made to improve the accuracy of these results in view of the possibility that a small percentage of titanium was combined with an impurity in the arc-melted powder. If this is in fact the case, the eutectoid and solubility figures reported above would be slightly too high in titanium content.

4. THE $\alpha \rightarrow \beta$ CHANGE

In the dilatometric investigation, the $\alpha \rightarrow \beta$ transformation temperature could be detected in alloys containing 0–30 at.-% titanium, and the results on fifteen specimens are given in Table I. No significant alteration of the $\alpha \rightarrow \beta$ transformation temperature from that of pure uranium is apparent from these results.

From results on alloys made from bar and powder, it appears that the solubility of titanium in α -uranium at 650° C. is lower than the solubility in β -uranium at the eutectoid temperature. For the reasons previously mentioned, no closer determination of the solubility in the α -uranium phase has been made, but the specimens examined metallographically (Fig. 4 (b)) put the figure at <1 at.-% titanium at 650° C.

The solubilities of titanium in α - and β -uranium and the $\beta \rightarrow \gamma$ eutectoid composition reported by the American workers¹⁻³ are in close agreement with the results obtained in this investigation from bar-uranium specimens. Consequently, it seems probable that some loss of titanium from solid solution on alloying has influenced these workers' results.

The presence of β in an alloy containing 10 at.-% titanium at 690° C. has been confirmed by high-temperature X-ray photography. No specimens have been found in which the β phase was retained at room temperature. A typical ($\beta + \epsilon$) structure is shown in Fig. 8 (Plate LXXIV). This was prepared by reheating homogenized specimens at 700° C. for 21 days and water-quenching. The transformed β phase is of low titanium content, and stains readily by atmospheric oxidation to a dark-blue colour. On etching for 5 min. in nitric acid and acetic acid, the ϵ phase appears darker in the microstructure than the transformed β .

5. THE $\gamma + \epsilon$ REGION

Alloys in the composition range 4–84 at.-% titanium deposit ϵ from the γ solid solution on cooling. The effect of the loss of some titanium from the γ phase was also apparent in this region, as the composition of the compound appeared to be shifted from the ideal ratio to about 36 at.-% titanium. This effect was evident in metallographic specimens water-quenched from temperatures ranging between 880° and 650° C.

The form of the deposit of the compound in high-uranium alloys is illustrated in Fig. 9 (Plate LXXIV). The compound shows a marked tendency to form regular hexagonal-shaped crystals in the microstructure.

High-titanium solid solutions do not deposit ϵ in the regularly shaped masses found in high-uranium alloys. Fig. 10 (Plate LXXIV) shows a 60 at.-% titanium alloy after 7 days at 850° C., in which ϵ is precipitated through the γ grains and along the grain boundaries.

The compound ϵ is precipitated from the γ solid solution with a considerable contraction in volume. In the dilatometric investigation, this resulted in a marked change of slope of the curves when ϵ is precipitated on cooling, or when solution of the ϵ phase is complete on heating. The results on nine alloys in the range 10–70 at.-% titanium are given in Table I.

All dilatometer results bracket the $\gamma/(\gamma + \epsilon)$ boundary as determined metallographically. The hysteresis between heating and cooling in alloys in the region of the compound was about 10° C. At lower temperatures of precipitation of ϵ from the γ phase, the hysteresis is greater, e.g. 24° C. for an alloy containing 70 at.-% titanium.

6. THE COMPOUND U_2Ti

The structure of the intermediate phase U_2Ti (ϵ) has been determined from powder photographs.¹³ It crystallizes in the hexagonal $C32$ (AlB_2) structure, with $a = 4.828$ and $c = 2.847$ Å.

Dilatometry of alloys of composition corresponding to the compound shows that ϵ is deposited from the γ solid solution with a linear contraction of 1.0–1.2%. This is in close agreement with the difference in room-temperature X-ray densities, taking the lattice parameter of the γ phase at 33 at.-% titanium as 3.41 Å.

The ϵ phase was detected in powder and glancing-angle photographs of alloys in the range 10–95 at.-% titanium after quenching from 650° C., and in alloys containing 20–65 at.-% titanium, after quenching from the γ field. In the latter range, the γ phase could not be retained on water-quenching, and the transformation $\gamma \rightarrow \epsilon$ on rapid cooling often led to radial cracking of alloy beads near the composition of the compound, as a result, presumably, of the large volume change accompanying the transformation and the inherent brittleness of U_2Ti .

On etching in 1:1 nitric acid and acetic acid mixture, the ϵ phase darkens slowly to a yellow or brown colour, more rapidly than does α or transformed γ and

β . The oxide particles sometimes form similarly shaped masses to the ϵ phase, but are readily distinguished after etching by their blue-grey appearance in the microstructure. After etching in the above reagent, specimens containing a high proportion of ϵ lack contrast between the ϵ grains, but the grain structure is well revealed under polarized light.

No evidence has been obtained to suggest that the ϵ phase exists over a wide homogeneity range, as reported by certain American investigators.^{2,3} Alloys containing 32–44 at.-% titanium have been examined metallographically, at 2 at.-% intervals, after annealing at 850°, 750°, 700°, and 650° C. and water-quenching. Before the annealing treatments, the alloys were homogenized for 4 weeks at 950° C. and quenched. As previously mentioned, the composition of the compound appeared to be shifted to about 36 at.-% titanium owing to some loss of titanium, but all alloys examined were interpreted as having two metallic phases present.

Powder specimens from previously heat-treated lump specimens containing 25, 32, 38, and 45 at.-% titanium were reheated to 650° C. for 24 hr. in thin-walled silica capsules *in vacuo* and water-quenched. No significant change in lattice parameter could be detected in any of these specimens or in specimens with 32 and 38 at.-% titanium water-quenched from 750° C.

Consequently, it is considered that the compound ϵ exists over only a narrow homogeneity range, very near to the ideal composition. Metallographic and dilatometric examination indicates that it is formed from the γ solid solution at $898^\circ \pm 3^\circ$ C.

7. THE $\gamma \rightarrow \delta + \epsilon$ EUTECTOID

The eutectoid change in high-titanium alloys was sluggish. It could not be detected dilatometrically, and considerable hysteresis was found in lump specimens annealed at temperatures near the eutectoid.

Powder specimens of alloys in the composition range 75–95 at.-% titanium, taken from γ -homogenized and quenched samples, were annealed in thin-walled silica capsules and water-quenched. Equilibrium in lump specimens at the annealing temperatures in the vicinity of the eutectoid was attained by cold rolling before each annealing treatment. Alloys with 76 at.-% titanium could be worked to about 20% reduction, and alloys with 84 at.-% titanium to about 50% before cracking started. Metallographic and glancing-angle X-ray examinations of these specimens confirmed the results given by the powder specimens, and have placed the eutectoid transformation at $655^\circ \pm 5^\circ$ C., 83.0 at.-% titanium.

8. THE $\gamma + \delta$ REGION

Microstructures of typical alloys from this region are shown in Figs. 11 and 12 (Plate LXXIV). Both contain the δ phase (α -titanium) as the lighter-etching constituent, in conjunction with partially transformed

γ . In the 99% titanium alloy water-quenched from 850° C., the acicular nature of the transformed γ is evident. The $\gamma/(\gamma + \delta)$ boundary was determined by metallographic examination of annealed specimens of this type.

The solubility of uranium in α -titanium at 650° C. was determined by metallography and by an auto-

of these specimens was rendered difficult owing to a "peppery" appearance of the titanium grains after etching. This type of structure has been attributed by previous workers to hydrogen in the titanium alloys examined. The metallographic results indicate, however, that the solubility of uranium in α -titanium at 650° C. is small.

The autoradiographic experiment indicated a solubility of 0.7–0.8 at.-% uranium at 650° C. The results of a series of track counts across the diffused zone are given in Fig. 13. A standard homogeneous alloy specimen containing 0.5 at.-% titanium was exposed simultaneously with the diffused specimen on the nuclear plate, and the track count from this specimen was used in the calculation of the solubility.

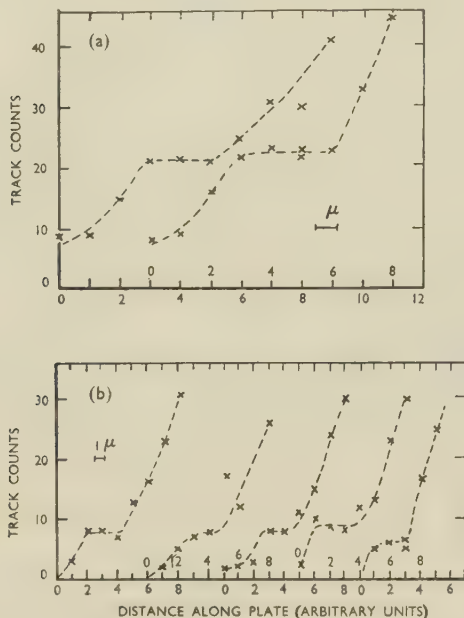


FIG. 13.— α -Track Count from Uranium-Titanium Diffusion Couple.

Standard count for 0.5 at.-% uranium specimen (a) 13 tracks, (b) 6 tracks.

radiographic experiment. Small arc-melted ingots containing 0, $\frac{1}{2}$, 1, and $1\frac{1}{2}$ at.-% uranium were cold rolled to 50% reduction, packed in titanium turnings in an evacuated silica tube, and homogenized at 950° C. for 7 days. The alloys were quenched, given a further 50% reduction by cold rolling, reheated to 650° C. for 7 days, and again quenched. The fact that these treatments resulted in no increase in the final hardness of the unalloyed titanium sample was taken to indicate that the contamination of the specimens during the treatments was small. The metallography

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REFERENCES

1. R. W. Buzzard, R. B. Liss, and D. P. Fickle, *J. Research Nat. Bur. Stand.*, 1953, **50**, 209.
2. M. C. Udy and F. W. Boulger, *U.S. Atomic Energy Commission Publ.*, 1952, (BME-774).
3. M. C. Udy and F. W. Boulger, *Trans. Amer. Inst. Min. Met. Eng.*, 1954, **200**, 207.
4. R. L. Berry, W. G. Henry, and G. V. Raynor, *J. Inst. Metals*, 1950–51, **78**, 643.
5. D. H. Bangham and R. E. Franklin, *Trans. Faraday Soc.*, 1946, **42B**, 289.
6. G. A. Geach and D. Summers-Smith, *J. Inst. Metals*, 1951–52, **80**, 143.
7. C. W. Tucker, Jr., *Acta Cryst.*, 1951, **4**, 425.
8. A. S. Wilson and R. E. Rundle, *ibid.*, 1949, **2**, 126.
9. B. W. Levinger, *Trans. Amer. Inst. Min. Met. Eng.*, 1953, **197**, 195.
10. Z. S. Basinski and J. W. Christian, *J. Inst. Metals*, 1951–52, **80**, 659.
11. J. S. Bowles, C. S. Barrett, and L. Guttman, *Trans. Amer. Inst. Min. Met. Eng.*, 1950, **188**, 1478.
12. A. U. Seybolt and H. T. Sumsion, *ibid.*, 1953, **197**, 292.
13. A. G. Knapton, *Acta Cryst.*, 1954, **7**, 457.

SOME OBSERVATIONS ON CONSTITUTIONAL CHANGES IN COPPER-ALUMINIUM ALLOYS AT TEMPERATURES BELOW THAT OF THE $\text{BETA} \rightleftharpoons \text{ALPHA} + \text{GAMMA}_2$ EUTECTOID*

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SYNOPSIS

Prolonged annealing experiments have been carried out on binary copper-aluminium alloys containing 8.7–16.5 wt.-% aluminium at temperatures in the range 340°–400° C. Microscopical and X-ray evidence has indicated the existence of an additional stable phase in the copper-aluminium system. It is suggested that this phase forms as the result of a peritectoid reaction between the α and γ_2 phases. The temperature of the suggested peritectoid reaction lies within the range 350°–400° C. Isothermal-transformation experiments have confirmed these findings.

I.—INTRODUCTION

THE copper-aluminium constitutional diagram shows,¹ within the composition range 9.4–15.6 wt.-% aluminium, a eutectoid reaction at 565° C., in which the high-temperature β phase decomposes into the α and γ_2 phases. Below this temperature α and γ_2 are reported as the only stable phases. However, by analogy with the copper-tin system, and taking account of certain phenomena reported to occur in copper-aluminium alloys at temperatures below that of the eutectoid, it appears possible that the $(\alpha + \gamma_2)$ eutectoid aggregate may be stable only over a limited temperature range.

The copper-tin system,² like that of copper-aluminium, has a body-centred cubic, high-temperature β phase, which decomposes into α and δ . In both systems the α phases are face-centred cubic solid solutions. The δ phase of the former system and the γ_2 phase of the latter both have γ -brass-type structures. The δ phase of the copper-tin system decomposes eutectoidally at approximately 350° C., but no such decomposition of the γ_2 phase in the copper-aluminium system has been reported.

Haynes³ reported unusual microstructural features in a copper-aluminium alloy containing 12.2 wt.-% aluminium, isothermally transformed below about 400° C. In a specimen transformed for a period longer than 5 days at 350° C., a duplex precipitate was observed at some grain boundaries. The quantity of the precipitate increased with transformation time, approximately 15% being present after 5 weeks. On etching with ammonia and hydrogen peroxide, the precipitate was seen to consist of ragged bluish-coloured particles in a pink matrix which showed twinning. Haynes suggested that this structure

might be particles of γ_2 in α solid solution supersaturated with aluminium.

Greninger⁴ has investigated the tempering of martensitic structures in copper-aluminium alloys at temperatures up to 350° C. X-ray examination of a martensitic 13.2 wt.-% aluminium alloy heated for 20 days at 350° C. showed little change from the pattern of the martensitic structure. Greninger suggested that, if the equilibrium state for the alloys at all temperatures below that of the eutectoid is an $(\alpha + \gamma_2)$ structure, then a tempering treatment of 20 days at 350° C. should allow substantial decomposition of the martensite into these two phases.

There appears to be no reference in the literature to the annealing of $(\alpha + \gamma_2)$ structures to investigate the possible formation of an additional phase in the copper-aluminium system.

II.—EXPERIMENTAL METHODS

The compositions of the alloys used in the investigation were:

Alloy No.	1	2	3	4	5
Al, wt.-% (nominal)	8.7*	10.7	12.4	14.2	16.5

* Analysed.

The alloys were made from electrolytic copper and aluminium of 99.99% purity, in the form of small chill-cast bars. The bars were hot worked, with the exception of alloy 5, and were annealed at 800° C. for a minimum of 20 hr.

Samples of the annealed alloys were then treated to produce equilibrium structures at 520° C. In the case of alloys 3, 4, and 5, this involved heating to about 850° C. for $\frac{1}{2}$ hr., slowly cooling through the eutectoid

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transformation temperature to 520° C., and holding at that temperature for about 20 hr., followed by air-cooling. For alloys 1 and 2 it was found necessary to give a longer heat-treatment to obtain α phase of equilibrium composition at 520° C. (viz. cooling slowly from 850° to 580° C., just above the eutectoid temperature, and then cooling over a period of 1 week from 580° to 520° C.).

Microscopical examination showed that these "stabilizing" treatments had decomposed all the β phase present at high temperatures. Measurements of α -phase lattice parameter on alloys 2 and 4 gave a value of 3.657 kX. This is in agreement with values given in the literature for saturated α phase.^{5, 6} With regard to alloy 1, microscopical and X-ray examination of powder samples confirmed that it consisted entirely of α phase. The lines of the diffraction pattern were sharply defined, indicating uniformity of composition within the α phase.

Samples of the "stabilized" alloys were then annealed at temperatures ranging from 340° to 400° C. for periods of up to 6 weeks, with a temperature control of the order of $\pm 5^\circ$ C., and these samples were examined microscopically.

Filings were obtained from the "stabilized" alloys 1, 2, 4, and 5. These were sealed in evacuated glass tubes, and given a stress-relief treatment of 1 hr. at about 450° C. Samples of the filings were examined by X-ray diffraction after this treatment; other samples were annealed at either 340° or 400° C., for periods of up to 6 weeks, before examination. A 19-cm. camera with Cu K_α radiation was employed.

One of the authors (D. L. T.) has also studied the isothermal decomposition of the β phase in binary copper-aluminium alloys within the composition range 11.3–12.4 wt.-% aluminium. Specimens transformed for periods of up to 11 days at either 350° or 400° C. have been examined by microscopical and X-ray methods.

II.—EXPERIMENTAL RESULTS

1. MICROSCOPICAL EXAMINATION

(a) Samples Annealed at 340° C.

Whereas alloys 1 and 5 showed no change in micro-structure from that of the stabilized condition, alloys 2, 3, and 4, after etching with chromic acid,⁷ exhibited two new features:

(1) Particles of a pink-etching phase had formed within the ($\alpha + \gamma_2$) eutectoid areas, and had grown by partial or complete absorption of both the α and γ_2 phases in these areas. The pink-etching phase was not detected within pro-eutectoid areas of either α or γ_2 . After annealing for 6 weeks at 340° C., the amounts of the phase detectable were relatively small, but in a sample annealed for about 6 months up to approximately 30% of the eutectoid had changed to the new phase. Fig. 1 (Plate LXXV) illustrates the structure of alloy 4 after annealing for 6 months.

(2) The α phase in the eutectoid, and also the pro-eutectoid α in hypo-eutectoid alloys, etched darkly, the effect being suggestive of the formation of a precipitate within the α phase. Preliminary experiments had been carried out with samples of alloy 2 which had not been brought to complete equilibrium at 520° C., slight composition gradients existing in the pro-eutectoid α areas. In these specimens the dark-etching feature produced a "coring" effect in the pro-eutectoid α areas, as shown in Fig. 2 (Plate LXXV), the darkening or pitting being strongest within the α adjoining the γ_2 phase, and decreasing towards the centres of the pro-eutectoid areas.

(b) Samples Annealed in the Range 350°–370° C.

Traces of the pink-etching phase were detected in samples annealed at 350° C., and the dark-etching feature was obtained on annealing up to 370° C., although it was not as marked as in samples annealed for comparable times at 340° C.

(c) Samples Annealed at 400° C.

The structures were similar to those of the "stabilized" alloys.

(d) Samples Isothermally Transformed at 400° and 350° C.

During transformation of an alloy containing 11.3 wt.-% aluminium at 400° C. (i.e. about 50° C. below the M_s temperature), the pink-etching phase formed as an intermediate transformation product, but it tended to decompose into a mixture of the α and γ_2 phases. Transformation of three alloys within the composition range 11.3–12.4 wt.-% aluminium at 350° C., produced the pink-etching phase, and this appeared to absorb any ($\alpha + \gamma_2$) aggregate which had previously formed. In all three alloys, the stable structure at 350° C. seemed to consist of the pink-etching phase plus the γ_2 phase. The structures produced by isothermal transformation appear to be similar to those obtained by Haynes,³ except that the twinning effect which he noted has not been observed.

2. X-RAY EXAMINATION

(a) Samples Annealed at 340° C.

The patterns obtained from samples of alloys 2 and 4 annealed for 3 weeks at 340° C. showed two new features as compared with the patterns from the "stabilized" samples:

(1) The presence of several additional weak lines at the low-angle end of the films. These lines could not be indexed on either the α or γ_2 patterns.

(2) A broadening of the higher-angle lines of the α -phase pattern, the effect being particularly marked in the (331) and (420) doublets.

A pattern from a sample of alloy 1 annealed for 9 days at 340° C. showed no lines additional to those of the α phase, but a slight broadening of the higher-angle lines was noted. Annealing a sample of alloy 2

for the same period produced the additional lines, and also the marked broadening effect of the (331) and (420) doublets of the α -phase pattern.

Annealing a sample of alloy 5 for 6 weeks at 340°C . produced no change in the pattern, that of the γ_2 phase being maintained.

(b) *Samples Annealed at 400°C .*

The patterns obtained were the same as those from the "stabilized" samples.

(c) *Sample Isothermally Transformed at 350°C .*

A sample of an alloy containing 11.3 wt.-% aluminium, transformed for 11 days at 350°C ., gave a pattern showing lines which corresponded approximately with the additional lines noted above.

IV.—DISCUSSION AND CONCLUSIONS

The experimental evidence indicates the existence of an additional stable phase (provisionally designated X) in the copper-aluminium system (Fig. 3).

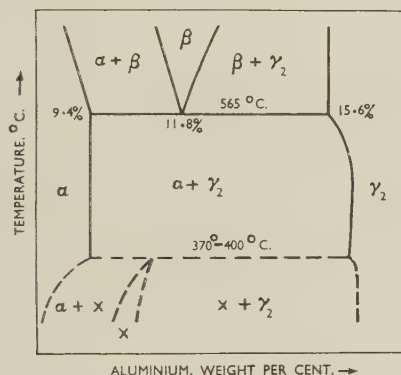


FIG. 3.—Suggested Form of Copper-Aluminium Equilibrium Diagram in the Approximate Range 8–17 wt.-% Aluminium.

The fact that the phase grows by absorption of both α and γ_2 phases suggests that its mode of formation is by a peritectoid reaction between these phases. Since no trace of the phase was found in alloy 5, the possibility of a eutectoidal decomposition of the γ_2 phase can be eliminated.

The composition of the new phase cannot be accurately stated from the available evidence. The

observation that alloys containing 11.3–12.4 wt.-% aluminium, isothermally transformed at 350°C ., tended to attain a structure containing γ_2 in addition to the pink-etching phase suggests that, at this temperature, the latter contains less than 11.3 wt.-% aluminium.

It is considered that the change in the etching characteristics of the α phase, and the broadening of the higher-angle lines of the α -phase diffraction pattern, noted after annealing ($\alpha + \gamma_2$) structures at 340°C ., may be due to a decrease in solubility of aluminium in the α phase below the peritectoid temperature, with an accompanying precipitation of the new phase. The slight broadening of the α -phase lines noted after annealing a sample of alloy 1 at 340°C ., suggests that some precipitation may have occurred, indicating that the solubility of aluminium in α may be less than 8.7 wt.-% at 340°C . However, no confirmatory microscopical evidence was obtained.

With regard to the temperature of the peritectoid reaction, available evidence does not allow this to be fixed within close limits. The structures of isothermally transformed alloys, and those resulting from annealing ($\alpha + \gamma_2$) aggregates suggest that the peritectoid temperature lies within the range 350° – 400°C .; it is probably between 370° and 400°C .

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REFERENCES

1. G. V. Raynor, *Inst. Metals Annotated Equilib. Diagr. Series*, No. 4, 1944.
2. G. V. Raynor, *ibid.*, No. 2, 1944.
3. R. Haynes, *J. Inst. Metals*, 1954–55, **83**, (7), 357.
4. A. B. Greninger, *Trans. Amer. Inst. Min. Met. Eng.*, 1939, **133**, 206.
5. A. J. Bradley and P. Jones, *J. Inst. Metals*, 1933, **51**, 131.
6. I. Obinata and G. Wassermann, *Naturwiss.*, 1933, **21**, 382.
7. W. C. Coons and D. J. Blickweide, *Trans. Amer. Soc. Metals*, 1945, **35**, 284.

Discussion

The Control of Quality in the Production of Wrought Non-Ferrous Metals and Alloys. III.—The Control of Quality in Heat-Treatment and Final Operations *

Dr. A. R. E. SINGER † B.Sc., (Member) (*rapporteur*): This Symposium is the third of a series dealing with the control of quality in the production of wrought non-ferrous metals and alloys, and it includes six papers on heat-treatment and final operations. The first of the series, held in 1953, covered melting and casting, while last year there was one concerned with working operations, so that the present Symposium forms the logical conclusion of the series.

I think it appropriate to compare the contents of the present papers with those of the papers submitted in previous years. There are many ways of comparing papers, and I have chosen one which in my opinion is suited to the case before us and brings out one of the aspects of control in which many of us are particularly interested.

In practically every instance in the seventeen papers which are involved we find that the contents are separable into two main parts. The first concerns the equipment that can be used for the fabrication of non-ferrous metal products, the practical precautions that have to be taken in order to ensure a product of acceptable quality to the commercial world, and the methods of testing or inspection appropriate to that product. In other words, the essential "know-how" of the manufacture of non-ferrous metals. The second part, which perhaps has not been dealt with in quite so much detail, is the institution of measures, or the setting up of systems, for controlling quality.

As regards the first part, i.e. the essential know-how, there is before us a great wealth of technical information. We are presented with an enormous range of ideas as regards equipment and techniques. As examples, procedures are shown, and practical recommendations detailed, for straightening copper bars and tubes, or techniques are described for revealing cracks that may exist in finished light-alloy forgings. We are, in fact, given all the essential technical data that it is necessary to comprehend in order to be able to turn out products of good quality from the factory.

We ought to recognize that this has been made possible only by the generous attitude of all the companies associated with the papers that we are considering. They have given this information without reserve, and in particular we may take pride in the fact that all this knowledge and technical data, much of which has appeared for the first time, has been made available to the world through the medium of the *Journal* of the Institute of Metals. We should bear this in mind, because in many cases it has perhaps meant a good deal of sacrifice by the concerns connected with the papers.

This technical information was badly needed by industry, and in all probability it has already made quite a difference to our methods in the factory. I hope that through the present Symposium we shall be able to introduce still more of these ideas and in the future to improve our techniques even further. To be of any value, however, the data must be of a detailed nature, which necessarily means of localized interest, and while the interchange of information helps in the spreading

of ideas between different groups of people interested in different metals and processes, each group tends to employ techniques which are not wholly applicable in other fields. Bearing this in mind, it is not surprising that no natural order is apparent in the technical data dealing with these various aspects of the subject. I intend therefore, to mention only certain special features covered by the authors of each paper.

The paper by Dr. Shilling deals principally with aeronautical inspection, and the author outlines the administrative procedures and the methods of working adopted by the Aeronautical Inspection Directorate. My attention was caught by three sentences on p. 194 of the paper: "The tests called for in the specification do not always yield results that are of direct use to the designer. It must be remembered, however, that the aim of a specification is to provide uniform material. The designer's requirements can be catered for elsewhere."

The most important point here is the statement that "the aim of a specification is to provide uniform material". Quite often we tend to lose sight of this, because most specifications are couched in terms of minimum requirements. However, if we realize that they are so worded mainly in order that progressive manufacturers can make the maximum use of the opportunities thus afforded for improving their product, then it will be seen that in reality the purpose of a specification is to ensure material of uniform properties, and consequently it can be considered as a part of a controlled process. Standards, in other words, form only one branch of a wider system of control, and are not complete in themselves.

Of particular interest in the paper by Mr. Field and Mr. Salter is the grain-size assessment based upon Erichsen tests, giving a quick method for the long-term control of grain-size. This method has obviously been available to us for many years, but it is interesting to learn of its use for control purposes. Again, there is a reference to partial annealing, or temper-annealing, or letting-down. Here we have a controlled annealing process in which the procedure is partially to anneal material in the hard-rolled condition so as to obtain an intermediate hardness. This process deserves a great deal more attention than it seems to have received, because, given control measures such that we can be quite certain where we are with these intermediate hardnesses, it is likely to yield very big economies in manufacture.

The papers by Mr. Miller and by Mr. Hysel and Mr. Collier discuss the annealing and heat-treatment of copper and copper alloys on an industrial scale, paying special attention to problems of bright annealing, and, in the latter paper, to stress-relief by annealing.

Mr. Edmunds and Mr. Lloyd are concerned with the control of quality in the production and heat-treatment of light-alloy forgings. There is a very interesting section on the choice of forging stock in relation to the size and the properties required in the final product. Some valuable data are given

* Joint discussion on papers Nos. 1589-1594 (*Journal*, this vol., pp. 193-270) held in London on 31 March 1955. Part I of the Symposium took place on 25 March 1953 and Part II on 28 April 1954, and the papers and discussions are printed

in Vol. 81 and Vol. 82 of the *Journal*, respectively.

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on the avoidance of distortion and internal stress by quenching the light-alloy forgings from the heat-treatment temperature in water held at various temperatures, and on the resulting mechanical properties.

Dr. Betteridge and Mr. Cound deal with nickel and nickel-base alloys. Here the metallurgy is quite different, and, as one would expect, the methods of control are unconventional. But this very fact offers the opportunity of profiting by a study of different ideas. In their factory great use is made of inter-stage examination during manufacture, or of process inspection, and many special testing methods and a number of novel simulated tests are employed. Some hard things have been said about simulated tests, but as a means of controlling processes they are undoubtedly of great value. This paper will repay study and examination, for the ideas put forward may well be applicable to the aluminium- and copper-base alloy fields.

Turning to the other aspect of the papers, we have the setting-up of systems of control in connection with the manufacture of non-ferrous metal products. By this I mean first of all the establishment of a standard of quality which must be compatible with the economics of manufacture. Then, the determination of some means of attaining this standard and correcting any deviation from it that may occur owing to changes in process variables. It was generally recognized in the earlier papers that considerable economic benefits could result from utilizing to the maximum degree such true systems of control, and in the first two sections of the Symposium many examples were quoted of that being done. In the third section we have rather fewer examples of control of this kind, and it is natural to ask the reason for it and to consider whether it is necessarily true.

Part of the answer may be that frequently in these finishing operations we are dealing with mechanical processes, which as a consequence may not be so amenable to metallurgical control as are melting, casting, or working processes. I believe, however, that finishing operations are not unsuited to control methods. The main trouble is that the full potentialities of control—used in its strict sense—in such operations have not been realized, but the adoption of more control measures would undoubtedly lead to lasting benefits in the field of non-ferrous metallurgy.

Mr. S. S. SMITH,* M.Met. (Member of Council): When he presented the first paper in this three-part Symposium on the Control of Quality in 1953, Dr. Singer defined the principles and application of statistical quality control. I must confess that I have the feeling that, to quote Walter Scott in "*The Bride of Lammermoor*", there has been a tendency for you to "close your ears to the voice of the singer". The point of view which Dr. Singer then expressed probably did not receive the attention it deserved. Only two subsequent papers included serious mention of the subject. None in the latest series has done so, and I wonder whether the producers of non-ferrous metals have given adequate consideration to the matter. It may have little significance when one is concerned with ingots and the count is small, but are matters not different when the count is higher, as it inevitably is, when finishing operations are involved? The present section is, in fact, concerned with annealing and finishing, so that the consumer, or rather his inspector, must not be overlooked. He might well be better satisfied if statistical quality control were used as a guide to maintaining uniformity in the product he is to receive.

Mr. Bond-Williams, in opening the discussion on the set of papers comprised in Part I of the Symposium, discussed the consumer/producer relationship, and argued that there should be a definition of, and acceptance of, an ideal measure of quality, but he agreed with Dr. Singer that control can be effective only when the elements of quality have been standardized and rendered capable of numerical measurement. A

clear distinction has been drawn by Dr. Singer between control and activities concerned with investigating an unstable process and with making appropriate modifications to a process. The latter is process investigation, and has formed the main content of the past and present papers. This has been put in another way by Mr. Kasz, who, speaking on 28 April 1954, thanked authors for advancing knowledge of what we do but wished that greater emphasis had been laid on control of what we do. This mild reproof is still perhaps operative, and I certainly feel that Mr. Kayser was right when, on a previous occasion, he argued that statistical methods must be used by the men in the works, for without control of this kind two inspection departments are necessary, one at the producer end and the other at the consumer end.

To cut down duplication of this kind, there is need for a free exchange of views between the two parties to the transaction. Throughout previous papers and the attendant discussions, which I have re-read with great interest, it has been accepted that the agreed aim need not necessarily be a product capable of maximum performance, but one appropriate to end use and capable of being turned out at an economic price. Professor Murphy put this well when indicating that the tolerance allowable from the standard of reference is dictated not only by the importance of the property in question but also by the cost of exercising control within the fixed limits of tolerance.

It is evident that there must never be control for its own sake, but that effective control, whether automatic, statistical, operational, or dependent on the skill and integrity of the operator, must be directed to the prevention of error. Dr. Shilling, in an admirably objective fashion, has defined the requirements under a number of broad headings. He has also dealt with inspection procedures in general terms, and has provided a useful touchstone by which the succeeding papers, in some aspects at least, may be judged. Taking one aspect only—probably the simplest—which he has discussed: control of chemical composition. A brief reference is made in some of the papers to this subject, but there is little comment on the standards and accuracy of the control procedures involved or on the specifications, as such, with which the writers are concerned. I conclude, in fact, that Mr. Kasz is right, and that the treatment accorded by present and past writers is based on disclosures of knowledge of what we do rather than how we control what we do.

I should like to express agreement with Dr. Singer that, in describing what is done, great generosity has been displayed by the firms concerned. It is, indeed, a tribute to the enlightenment of the authors, and of their employers, that such free and frank statements can be made.

I should like now to comment on individual papers, selecting for special attention two features, namely, surface finish and the tools used in achieving that finish.

Mr. Field and Mr. Salter have touched upon details often neglected in describing how finish is maintained. They have, for instance, advocated that the burr on the leading edge of sheets from the flying-shear and levelling operations should be uppermost when piling the sheets, so as to avoid scratching. They have, however, made certain operations appear too easy, although they recognize that many of them are characterized by a high labour content and thus are susceptible to deterioration with the quality of skill and of judgement. It follows, then, that responsibility for control of quality resolves itself into controlling the men doing the job, and that finishing departments should not be expected to rectify damage arising from earlier causes. Such corrections as can be effected must be regarded as incidental, and it must be realized that all additional handling presents new risks and certainly added costs.

I should like to put two questions to these authors. First, have they made use of devices such as those suggested by the Royal Aircraft Establishment for assessment of flatness

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in sheet? Secondly, have they any views on the use of controlled atmospheres to minimize staining of aluminium-magnesium alloys during annealing, or do they prefer flash annealing? In the paper an oxygen-free atmosphere is mentioned, but other authorities suggest that oxygen prevents staining by carbon. This subject of staining in heat-treatment is still of vital importance, even in salt baths, as witness the recent paper by colleagues of mine.*

Mr. Miller has also concerned himself with surface condition. At one point he mentions rough annealing and quenching as a means of improving surface, but would it not be well to use rolls capable of producing a fine finish? Does he and do the other authors pay due attention to their choice of tool materials? If so, this is not evident from the contents of the papers. This is a vital matter and one which the Institute and the B.N.F.M.R.A. are now looking into in a serious fashion. This is indeed a welcome development.

Mr. Miller discusses the use of die-scalping tools. Does he recommend their use in preparing stock for the making of co-axial tape, where a single sliver might adversely affect performance? Are all the tools used made up of known steel, heat-treated under standardized conditions, so as to ensure uniform cutting? Has Mr. Miller any idea whether drawing-die shape affects the extent of spring-back? This phenomenon is a considerable nuisance and is well discussed by Mr. Miller, who has, in fact, presented a paper made notable because he is, in effect, a consumer as well as a producer, and so has catered for both sides in preparing his contribution.

The customer point of view seems less evident in the interesting paper by Mr. Hysel and Mr. Collier, who have chosen to emphasize special materials rather than copper and brass, which represent the major output of the industry. What they have to say on their chosen topics is authoritative, although there is a tendency to over-simplify. For instance, the recommendations of Tables I, II, and III (p. 234) provide for no distinction between the requirements for coils of differing size or earlier history. Then there is reference (p. 235) to the fact that, in the production of 1.31-in.-wide copper strip, a lateral contraction of 0.0004 in. takes place, and that allowance should be made when preparing the cutters for slitting the hard strip before annealing. This certainly indicates that attention of a high order is paid to tools.

The nickel alloys are known to me only as a customer, but I am impressed by the description of the control methods used in their production by Dr. Betteridge and Mr. Cound. It is made apparent that, having regard to the prime cost of the materials involved, standards must be rigid, with ruthless rejection of faulty material at the earliest possible stage. I note that many of the test procedures are in line with those used for the less costly alloys of commerce, but that there exist also fascinating and highly specialized techniques. These include welding, spiralling, glass-bead, and other procedures, and the magnetic checking of nickel alloys. This appears to be highly successful, despite its inherent simplicity, and one can only wish that nature had perhaps made it more widely applicable.

On the subject dealt with by Mr. Edmunds and Mr. Lloyd again I have no specialized knowledge, but I revert to one of the two topics on which I said that I would comment—that is, tools and tool materials. The authors mention the need to pay attention to die design, but they give only a few details of the steels used. Their tools must be very costly. Are they treated with great care and what is, in fact a representative heat-treatment schedule? If all went well, a large number of products would come from the hammer, and here statistical analysis would surely be advantageous—yet it is not mentioned by the authors. Did they, in fact, use statistical quality control?

With the foregoing question, it will be noted, I have come

full circle and reverted to my opening remarks. I conclude by saying that it behoves suppliers to use the best available techniques and equipment to ensure that they satisfy their customers. I am pleased to note that all the authors have paid attention to packaging, as a final gesture to win the confidence of the customer, who is still "always right".

Mr. E. J. BRADBURY,† M.Eng., A.M.I.Mech.E., A.I.M. (Member): The first point that I want to make really arises from reading between the lines in Dr. Shilling's paper. Throughout the paper, the author implies that inspection must be carried right back to the very beginning of any processing. When inspection is carried out as far back as that, the A.I.D. must also lay down the grade of the processing to be undertaken, and I should like to question whether the inspection authority is then ethical in rejecting material which has been processed in accordance with its instructions. I think that in one or two parts of his paper Dr. Shilling does imply that that is the end towards which we are moving.

In his remarks on composition and analysis on p. 195, Dr. Shilling says: "The A.I.D. normally regards an accurate knowledge of composition as an essential starting point, for much can often be foretold or expected from such information." I am sure that most of us who have anything to do with the production of alloys know that many of the most important elements which are added to or eliminated from the materials we produce are not covered in specifications, and that to analyse for them on an inspection basis would involve quite considerable expense. I wonder whether the A.I.D. are deceiving themselves when they read the analysis sheets they obtain, and whether they should not rather just accept the certificate that the material is what it purports to be.

Another point has arisen recently where I think some revision in inspection procedure may be necessary. For some of the very special materials mentioned in the paper of Dr. Betteridge and Mr. Cound, the use of powder-metallurgy methods is leading to their being produced with enhanced properties, and these powder-metallurgy methods do necessitate the production of the materials in very small batches. If analysis of these small batches is to be carried out, it will involve a very considerable addition to the cost of the final product and an extension of analytical facilities. Some new method of dealing with that problem must be developed, and it may be that the authorities will inspect the product as it is supplied to the consumer and not involve themselves in inspection at earlier stages.

It is very interesting to compare the techniques that can be used with two materials, copper and nickel, as described in the papers by Mr. Miller and by Dr. Betteridge and Mr. Cound. These materials are handled in the works in a very similar way, and yet on p. 226 Mr. Miller points out that when strand-annealing copper the process is slow, presumably because it cannot be speeded up by the use of such variations as hydrogen atmosphere, and that the process, which is a very nice continuous one, can be employed only when other factors such as enamelling are involved. In the case of nickel wire, virtually all annealing is by strand-annealing, but of course there is no difficulty in the use of a hydrogen atmosphere with nickel, and production rates are not, comparatively, quite so high. Has Mr. Miller examined the possibility of eliminating some of these difficulties, such as sticking or discolorization, by the use of vacuum-annealing, and has he any comments to make on its possibilities?

Mr. Smith has mentioned that Mr. Edmunds and Mr. Lloyd do not discuss the die materials. I also would like to ask them whether they have any data regarding die life and how that is related to either the shape or the deformation that the material being forged receives, whether it is affected by the mass of the forging that is being handled or is influenced solely by the temperature that has to be used.

* E. C. Williams and H. J. G. Challis, *J. Inst. Metals*, 1953-54, 82, 465; discussion p. 641.

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Dr. G. E. A. BRAMLEY,* M.Sc. (Member): Dr. Shilling's paper gives a clear outline of the system of inspection adopted by the A.I.D. There is only one point upon which I should like to comment, and I trust my remarks will be taken as a suggestion and not a criticism. On p. 197 reference is made to the four conditions in which heat-treatable aluminium alloys may be found, but it will be seen that the designations used by the A.I.D. for the first two conditions, namely, "annealed" and "solution-treated and requiring no precipitation", are not those generally adopted by the aluminium industry or employed by the British Standards Institution. Would it not be possible for the A.I.D. to adopt the designations otherwise generally used and employ "O" for annealed instead of "A" and "T" instead of "N"? Many non-technical members of our own and customers' staffs are only now becoming acquainted with the significance of the various prefixes and suffixes with which we have adorned our system of designations. Every measure that can be taken to ensure the widest adoption and understanding of this system will be of benefit to all concerned.

Mr. Field and Mr. Salter mention many aspects which have a direct bearing on the control of quality in the production of aluminium and aluminium alloy wire—a form with which I am particularly concerned.

For instance, they detail (p. 207) the various factors affecting grain-size, in particular the effect of the degree of cold reduction before the final anneal or heat-treatment where, as far as possible, it is the practice to give reasonably heavy reductions to promote a fine grain-size after annealing. The same principle naturally applies in the drawing of aluminium alloy wire, but we have found that with certain heat-treatable alloys there are limitations which have to be applied to this principle. With modern multi-die continuous wire-drawing machines, it is practicable and indeed desirable, in order to secure their maximum utilization, to impose overall reductions in area of upwards of 80% from inlet to exit size. However, in attempting to do this with certain alloys, an upper limit of reduction in area, say, around 70%, has been found, beyond which, after solution-treatment, isolated large grains are encountered. The number and size of these coarse grains increase beyond this limit with increasing overall reduction in area. For a number of applications, especially for those where cold-forming operations are involved, such irregularities in grain-size are unacceptable. In these cases, it has therefore been necessary to control the reduction in area before the final heat-treatment within defined limits below this upper critical reduction, in order to maintain an optimum, uniformly fine grain-size. It would be interesting to hear whether any other member has experienced a similar effect in the production of either wire or sheet and strip.

The benefits of temper-letting-down, again described by Mr. Field and Mr. Salter (p. 208), have been found of equal advantage in the case of aluminium and aluminium alloy wire. With multi-die machines it is more economical to draw with the maximum possible reduction from inlet to finished size and then let-down to the intermediate temper, than to draw to an inter-anneal size and follow by an additional, one- or two-pass, temper-drawing operation. In my own Company, temper-letting-down has been applied particularly to the aluminium-magnesium alloys, where, in certain cases, the success of particular applications has been entirely dependent upon the increased ductility achieved with temper-let-down material as opposed to temper-drawn material. The production of intermediate tempers in aluminium alloy wires by letting-down is also advantageous from the point of view of the elimination of process damage, since the amount of inter-operation handling is reduced and a full annealing treatment is eliminated.

As mentioned in the paper by Mr. Miller (p. 231), temper-letting-down may also be of assistance in the production of an intermediate temper of electrical-purity aluminium wire for certain types of insulated cables. In this case, however, the

problem is somewhat more complicated, since it is desirable to heat-treat the wire on the steel stranding reels on which this wire is normally drawn direct and, unless special precautions are taken, the effect of the heat capacity of the steel can affect the uniformity of the partial anneal achieved.

The problem of "burnt-oil" stain after annealing is a serious one with aluminium and aluminium alloy wire, as it is with strip; it is perhaps even more prevalent with the thicker-gauge wires owing to the necessity for using relatively high-viscosity drawing lubricants. By using a thinner and more volatile lubricant, coupled with a lighter reduction on the last die, it is possible to minimize the amount of oil on the wire going to the furnaces, thereby reducing the incidence of staining.

Where annealed wire is to be flattened to strip, the presence of "burnt-oil" stain, even if only slight, is a serious handicap to holding reasonably close tolerances on the width of the strip. The presence of a carbonaceous deposit on the surface of the wire affects the friction in the roll-gap and thereby influences the degree of spread obtained.

It is believed that strand-annealing could be of assistance in this problem, and it would be interesting to hear from the manufacturers of strand-annealing plant of their experience in the application of such equipment to the annealing of aluminium and aluminium alloy wires in sizes ranging from about $\frac{1}{8}$ in. dia. down to 36 S.W.G. In connection with the annealing of copper wire, Mr. Miller (p. 227) mentions the method of strand-annealing in tandem with wire-drawing at speeds of 2000 ft./min. and upwards. It would be of particular value to have the views of the manufacturers on their experience of the application of this tandem method to aluminium and aluminium alloy wire.

It may be of interest to mention one particular problem encountered in the heat-treatment in coil of wire in certain naturally ageing alloys. After quenching it is difficult to remove all the water trapped between the laps, even with vigorous shaking. In endeavouring to produce these materials with a fairly high degree of uniformity of mechanical properties after a limited period of natural ageing, it has been found that where water is entrapped in a coil ageing is retarded until all the water has evaporated. Since it can take anything up to three days to ensure complete removal, the effect of this retarding action can be appreciated in the case of materials which are otherwise normally aged for five days before release.

Fairly large quantities of high-strength, heat-treatable aluminium alloy wire are supplied in straight lengths for machining in automatics. Here the material is solution-treated in coil, before straightening, and difficulties are sometimes experienced owing to the coil settling down under its own weight at the solution-treatment temperature, resulting in the formation of short kinks or even actual indentations where one lap crosses over another. Such kinks, once formed, cannot be removed in the usual type of spinner straightening machine and, for applications where a high degree of straightness is required, as, for instance, where the rod has to be centreless-ground, such kinks usually lead to rejections. No mention is made of this effect in any of the papers dealing with wire, either in copper or aluminium alloys, and it would be interesting to hear whether other producers have experienced similar difficulties and by what means they have overcome them.

On p. 222, Mr. Miller, dealing with choice of fabrication method, states that, in general, extrusion results in a superior surface condition of the drawn wire as compared with that produced from hot-rolled rod. Our own experience with aluminium and aluminium alloy wire would not support this comprehensive statement, provided due care and attention is given to the production of a good-quality hot-rolled rod. We should certainly say that today wire with the highest quality of surface finish can be produced from hot-rolled rod, and in the case of my own Company, where wire for high

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surface-quality applications was previously made from extruded rod, we are now regularly producing a superior product from hot-rolled rod.

In conclusion, I should like to comment on Mr. Miller's passing remarks on aluminium and aluminium alloy wire. One must conclude that the author's connection with the copper industry has led him to devote only a page and a half to aluminium and its alloys in wire form. Aluminium itself has now been drawn in wire form for over fifty years and its alloys for upward of twenty-five years, and the alloys are used in many diverse spheres of industry today. With the increasing use of aluminium for electrical purposes, especially in cables and conductors, increasing quantities are now being drawn in works which had previously handled only copper. We are familiar with the amount of copper dust present in these works, and in that connection a word of caution is necessary. There are on record cases of trouble being caused by such dust settling on aluminium wire when it goes into service, and it is very desirable to make sure that where the aluminium is drawn in works which are also drawing copper, the two metals are kept separate and that copper dust is not allowed to contaminate the surface of the aluminium.

Mr. H. T. ROBERTS,* A.I.M. (Member): Mr. Miller states that in the choice of fabrication methods there are two types of rod stock—rolled rod and extruded rod. In the case of rolled rod, the stock may be produced from two sources; it can either be rolled direct from as-cast billets or rolled from extruded Gothics or round bar. Purely from an economic point of view the former is preferable, and it is possible, by careful control of the casting technique, to obtain satisfactory rolled rod from most of the aluminium alloys required for wire-drawing.

However, if the rolling performance of the as-cast billets is such that surface cracking and splitting is experienced, then it is necessary to resort to rolled rod from extruded material. The use of this type of rod for wire production has a serious drawback, a point already mentioned by Dr. Bramley, since it introduces a grain-size problem, especially with heat-treatable alloys. We have found that with wire drawn from extruded rolled stock, the percentage reduction has in some instances to be limited to approximately 50% before heat-treatment or annealing, to avoid the incidence of coarse grain due to secondary recrystallization on solution-treatment. These remarks apply equally to rod drawn from extruded rod. On the other hand, reductions in area up to 75% can safely be given to alloys of a similar type drawn from the rod rolled from as-cast stock, without encountering any grain-size difficulties.

Surface preparation of these two types of stock involves skimming or scalping in the case of some of the as-cast billets, to remove exudations, whereas for the extruded Gothics and round bar etching checks are taken to ensure that the material is free from sub-surface or double-skin defects.

Mr. Miller has mentioned the improved surface appearance obtained on extruded rod. It is mainly this condition that justifies its choice for certain specialized applications of drawn wire where surface finish is of prime importance, for example anodizing-quality wire.

With reference to the paper by Mr. Field and Mr. Salter, I should like to deal with the aspect of degreasing as related to quality control of light-gauge, rolled-to-temper sheets intended for the container trade. The finished temper-rolled coils, which have been rolled on high-speed mills flood-lubricated with a light mineral oil, are cut to length on continuous light shear lines, which incorporate a degreasing operation.

The choice of degreasing medium poses a problem, and is largely governed by the following requirements. It should

be non-toxic, it should not impair the lacquer-adhesion characteristics of the material, it should preferably be odourless, and, of course, it should be inexpensive. Furthermore, it is essential that the surface of the sheet after degreasing should not be absolutely chemically clean or oil-free, since this condition would result in difficulty in stacking the sheet after shearing, with the resultant hazard of surface chafing. It will be appreciated that this type of sheet would also cause inconvenience to the consumer when feeding the sheet on automatic lacquering or blanking lines. Thus, a suitable degreasing medium which fulfils the above-mentioned requirements having been chosen, the efficiency of the degreasing must be controlled to impart to the sheet the desired surface frictional or slip properties.

Mr. J. FERDINAND KAYSER†: May I start by saying that I am interested only in mass production and this will influence everything that I say. I am delighted that Dr. Shilling's paper is the first in the list of papers in this Symposium, because the whole basis of economic mass production is detailed therein. The only objection that I have to the principles laid down by the A.I.D. is that their specifications are not sufficiently close. If I wished to produce really good cheap saucepans of an aluminium alloy, the material that goes into an aeroplane would not be good enough because it would not be sufficiently uniform. That is a point that cannot be stressed too often and too strongly. Dr. Singer, in dealing with Dr. Shilling's paper, appreciated that when he quoted the words from p. 194: "It must be remembered, however, that the aim of a specification is to provide uniform material".

Someone playfully said to me that the A.I.D. is a rejection department. Now, inspectors should not be required to reject anything, and it should be unusual for them to have to do so. It is the duty of the production department to pass along material that is satisfactory, and the final inspection is only a check.

To conclude, I would say that I was shocked at the view expressed in the paper by Mr. Field and Mr. Salter, that if the quality of a product has not been properly controlled in the early stages it is often impossible to rectify the damage in the heat-treatment and final operations. I would like to ask just one question: "Why should one try?" It should be returned to the department that spoiled it.

Dr. K. SACHS,‡ M.Sc., A.I.M. (Member): I have two specific questions to put to the authors of papers. The first is addressed to Dr. Betteridge and Mr. Cound and concerns a very minor point. I am intrigued by their very beautifully illustrated test for gas-free nickel (p. 268), in which they wrap the nickel wire in glass, soften the glass, and watch the bubbles. What gas content is normally necessary to produce these bubbles, and what is the minimum gas content which would still give a detectable indication with other materials?

My second question, addressed to Mr. Edmunds and Mr. Lloyd, concerns the surface finish on dies. Am I right in thinking that the hand-polishing of dies represents a fairly substantial proportion of the total cost? How much of the total cost of die production can be ascribed to hand-polishing, and how do they decide to what finish they want to prepare their die surface? Why does the die surface have to be particularly well polished? Why do they want a nice smooth surface? I can think of two reasons: one is that the die life is prolonged if there is less friction on the surface and the forging is easily removed from the die, and the other is that the customer prefers a shiny forging. Has any work been done on the effect of different surface finishes on die life? How is the surface finish measured—by Talysurf, coefficient of friction, or other methods? I hesitate to ask how one attempts to balance the cost of finishing a die against the customer's desire for a brightly finished forging.

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Mr. W. W. KEE,* B.Sc., F.I.M. (Member): Both Dr. Singer and Mr. Kayser have drawn attention to the very significant statement in Dr. Shilling's paper that the aim of a specification is to provide uniform material. I will only say that it is not merely a question of uniform material within a batch, or from one batch to another; what the user wants is to be able to buy material next June which is of the same quality as he is buying today. Far too often the producers overlook that aspect.

I should like now to pass to another aspect of specification, edgewise bow, which is referred to both in the paper by Mr. Field and Mr. Salter and in that by Mr. Hysel and Mr. Collier. On p. 205, Field and Salter state: "Therefore, straight-rolling is necessary, the usual limits of tolerance being 1 in. departure from the straight on 10 ft. length for general work, and $\frac{1}{4}$ in. on 10 ft. for high-class work." Hysel and Collier give $\frac{1}{2}$ in. on 6 ft. As far as I know, there is no specification covering edgewise bow, and this is becoming a very serious problem, particularly in industries where follow-on tools are used. I should be glad to know how Mr. Field and Mr. Salter take a sample for measuring the edgewise bow and what extra cost is involved in changing from 1 in. on 10 ft. to $\frac{1}{4}$ in. on 10 ft.

On pp. 218-219 of their paper, Mr. Field and Mr. Salter deal with the very difficult problem of surface quality. I am surprised to note that these authors say that a very large variety of inspection standards is observed in respect of surface quality. What are those standards? How many standards do they employ, how do they measure them, and for what end-uses do they make the division?

On p. 235, Mr. Hysel and Mr. Collier state: "In the production of copper strip of nominal width 1.31 in. for the manufacture of co-axial cable, the contraction in width which occurs is of the order of 0.0004 in., and allowance for this should be made when preparing the cutters for slitting the hard strip before annealing." Personally, I feel that that is carrying things a bit too far. Is it really a practical proposition to make allowance for 0.0004 in. shrinkage in the width of 1.31 in. strip?

On the same page, the authors refer to grain growth at high temperatures in chromium copper. This can certainly occur, but to what extent is the authors' experience influenced by uneven cold working or even by a critical amount of cold working? We have found that excessive grain growth can occur in chromium copper, arising from either of these causes. I should like the authors to provide a little more information on that point. Still on the subject of chromium copper, at the top of the second column on p. 236 Mr. Hysel and Mr. Collier say: "The heat-treatment consisted of a preliminary solution-treatment at 1000° C. for 15 min., followed by precipitation-hardening at 475° C. for 4 hr." Do they mean that the precipitation-hardening material was held at 475° C. for 4 hr? If so, I should have expected—unless certain impurities or other elements were present—that overageing would decidedly have occurred. It has been our experience that above 450° C. chromium copper is susceptible to overageing. However, we have found that the presence of other elements, for example, a small percentage of silicon or sulphur, retards the tendency and, in normal practice, almost inhibits it.

Mr. H. CHADWICK,† M.Sc. (Member): Mr. Edmunds and Mr. Lloyd have covered a very wide field in their paper on drop-forging of aluminium alloys, dealing with many aspects of production and its problems. I should like to take one of those problems and examine it in greater detail, that is, the occurrence of blisters on forgings manufactured from extruded stock, particularly those produced to specification L.64 or L.65.

In our opinion the blisters can be divided into four main types, namely, those arising from (i) faulty stock, (ii) insuffi-

cient lubrication in the die during the forging process itself, (iii) overheating during preheating or heat-treatment, and (iv) a reaction with the furnace gases during solution-treatment.

It is very difficult to decide on the cause of the blisters from their appearance on the surface of the forging, and it is misleading to try. Microscopic examination affords a ready means of differentiating between them, and once the causes have been established a cure can be effected. Each type of blister has its own characteristic appearance under the microscope, as is shown by Figs. A-E (Plate LXXVI).

The type of blister due to overheating can readily be demonstrated by deliberately overheating during solution-treatment. The forging shown in Fig. A (Plate LXXVI) was heat-treated in a laboratory furnace at 530° C., approximately 25° C. above the temperature required by the correct practice. The characteristic rounding of the grains caused by partial melting can be readily seen. The 25% nitric acid etch used on this specimen is well known for demonstrating the degree of overheating; in this case it is shown by the width of the light bands which cross the dark background.

Examination confined to blisters on heat-treated extruded sections reveals mainly two types in addition to that caused by overheating. First, there is the type referred to by the authors as double skin, an example of which is shown in Fig. B (Plate LXXVI). Its characteristics are that the skin from the blister is smooth-sided and of more or less uniform thickness, the discontinuity being visible below the surface even when it has not been raised in a blister. If this type of defect occurs on the corner of an extruded section, then the thickness of the skin will vary from point to point round that corner.

Blisters in the second group found on extruded sections (illustrated in Fig. C, Plate LXXVI) are caused by reaction with the furnace atmosphere during solution-treatment. Defects occur as regular cavities scattered some distance away from the surface. At certain points these cavities become larger and more numerous, joining up to produce a large blister. Either of these types of blister can also occur on forgings: in the first case if the forging is produced from faulty stock, and in the second case if the furnace atmosphere is reactive.

This leaves the fourth type, which so far as is known occurs only on forgings (Fig. D, Plate LXXVI). The authors describe it as an area of double skin formed locally during forging, and, as can be seen, its appearance under the microscope is very different from that of a double-skin blister resulting from defective stock, and there should be no difficulty in identifying it.

The majority of blisters on forgings are covered by these types, occurring either singly or in combination. In the case of blisters resulting from a single cause, those due to reaction with furnace gases and those originating from faulty stock do not show any evidence of overheating. When etched with nitric acid the structures are of a more or less even shade, with no light bands. At a still greater magnification, no signs of fusion can be detected.

At this point I should like to raise the question, mentioned by the authors, of extruded stock which shows that it has been overheated during the actual extrusion process (p. 260), and to ask for more information regarding the methods of casting and of extrusion. Is the fusion shown in Fig. 11 (Plate XXXV) due to overheating during extrusion or is it something that persists from the cast state? It would be interesting to see the same field after etching in nitric acid.

The blisters produced during forging show light veins associated with the blisters (Fig. E, Plate LXXVI). It is thought that these indicate that heat has been generated at the moment of impact along the planes of maximum deformation, overheating some of them. This does not result in a blister immediately, but does so during solution-treatment when there is more time for the blister to develop. Most of these

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cavities show such a light line at each end in support of this view.

In conclusion, I would say that on this basis of the subdivision of blisters it is possible, by taking appropriate precautions to reduce blistering to a very low level. In particular, I would draw attention to such remedies as adequate pyrometry in controlling the temperature of preheating and solution-treatment; the rejection or scalping of stock shown to be defective by caustic etching of a heat-treated section, preferably from the back end of the extruded length; the use of creosote as an inhibiting agent during solution-treatment, as mentioned by the authors; and effective lubrication during forging. In the case of this latter precaution, is one to apply the lubricant to the die or to the forging?

Mr. A. R. MARTIN,* B.Sc., A.R.S.M. (Member): Mr. Chadwick has dealt with one aspect of the paper by Mr. Edmunds and Mr. Lloyd. I wish to direct attention to some more general points.

Dr. Singer referred in his introductory remarks to the wealth of technical "know-how" presented by the authors. Forging is an individual process in which a strong element of art is involved, and I feel that perhaps the word "technical" should be in inverted commas in this instance. The inspection and control systems are also of an individual character. For this reason, my remarks will tend to the practical side, since I regard the paper itself as a very comprehensive statement of fact.

The authors' claim that the drop-forgers' art lies in the preparation of a "dummy" or "use" such that the work done in the dies is reduced to a minimum, is in many cases an understatement of the importance of this most critical stage. Shaping a piece of round or rectangular bar by hand or free-forging involves a considerable degree of skill, but at the same time the dimensions will be judged by eye, so that the result must be somewhat crude. Pre-forming dies, as mentioned in the paper, are the best and in many cases not necessarily the most expensive answer.

Inspection and the removal of defects between passes is implied in various sections of the paper, but is not given the prominence it deserves. I say this because the purpose of these remarks is to demonstrate that forging defects may be generated at the outset, and defects carried over from one stage to the next become progressively more and more difficult to detect and remove. An even more important aspect is that if defects discovered at a particular stage are recognized as being systematic, then the technique leading up to that stage should be modified.

Some form of surface preparation is essential for this inter-stage inspection. The paper mentions caustic etching, and we consider this by far the most effective and also the cheapest method. A surface preparation not referred to either by Mr. Edmunds and Mr. Lloyd or by Dr. Shilling is polishing followed by chromic acid anodizing, which is used on the more important aircraft forgings. This is extremely sensitive and imposes a very high standard indeed. Not all defects so discovered will be associated with a chromic acid stain; many will appear as black hairlines on the surface. It is also important that this form of inspection be carried out after heat-treatment; otherwise defects may be missed which will not be picked up until the component has been finished.

As a method of surface preparation, polishing is time-consuming and consequently expensive, but unfortunately to date there is no alternative. It would be very useful if the eddy-current method of surface-flaw detection known as the Sigmatest could be developed for this purpose. The method uses a probe, but the surface to which it is presented must be flat. To cope with contoured surfaces it would be necessary to provide a core of small diameter or one tapered to a point, and I should be interested to learn whether or not the instrument manufacturers are able to do this.

While on the subject of non-destructive testing, references are made in Dr. Shilling's paper and in the paper by Mr. Edmunds and Mr. Lloyd to the use of ultrasonic methods of detecting internal defects in forgings. In both cases the authors state that the cast-billet stage is the best at which to carry out ultrasonic flaw detection, and Dr. Shilling considers that it would be easier to pick up defects at this stage. This would be true of major oxide inclusions and cracks, and I take it that he had in mind that once the material had been forged it would be difficult to detect any type of defect by this method owing to the shape of the component. It is possible, however, that a very small spherical defect in a cast ingot could be discovered only by a very sensitive instrument. This point defect would be extended to a line during extrusion, and in the course of subsequent forging it could be spread sideways to give a ribbon-shaped defect of appreciable area in the finished component.

However, I do agree with the authors that the method is limited to forgings of relatively simple shape. The single-probe technique is by far the easiest to use on irregularly shaped forgings, and for detecting flash-line defects in larger forgings the shear-wave probe has proved very successful. This probe was originally developed to detect defects in seam welds in large-diameter pipes and chemical vessels.

With regard to the choice of a suitable material as a starting point for the manufacture of forgings, the long list of defects which may be associated with extrusions would suggest that this material is likely to be the least satisfactory. However, Mr. Edmunds and Mr. Lloyd have named it as perhaps the most suitable general-purpose stock for the production of smaller forgings. I would suggest that probably the majority of small and medium-sized forgings in this country are produced from such materials. Where longitudinal properties are of the greatest importance and the shape of the forging lends itself to production from this material, it is, of course, superior, and the outstanding example of such a case is the aircraft propeller blade.

The authors refer to the fact that the longitudinal properties of rolled bar are inferior to those of extruded bar, but they go on to demonstrate that the properties obtained from forgings are not significantly different whichever material is used. The results on rolled bar may therefore be regarded as a more realistic indication of what may be expected from the forgings.

The best combination of properties is undoubtedly achieved by tri-axial working of cast material on a press, as consideration of the following tensile properties obtained from typical forgings will demonstrate. Die forgings produced from extruded bar to D.T.D. 683 would have typical longitudinal properties of the order: 0.1% P.S. $32\frac{1}{2}$ tons/in.², U.T.S. 36 tons/in.², and elongation 13%. However, whilst the transverse P.S. and U.T.S. would not be reduced appreciably and the elongation would be two-thirds of the longitudinal value, the short transverse P.S. and U.T.S. would be 90-95% and the elongation only one-third of the longitudinal. Starting from tri-axially worked material, the longitudinal properties would be of the same order and the transverse and short transverse P.S. and U.T.S. values would not be reduced appreciably. Furthermore, the transverse elongation would be at least four-fifths of the longitudinal and the short transverse at least one-half.

In the case of hand forgings produced on open dies, this directionality is even less marked, although the general level will be slightly lower. But since components produced from hand forgings are shaped by machining and little control of the grain flow by forging is possible, the advantage is very considerable.

Mr. A. W. MATTHEWSON †: I speak as an inspector, and I should like to congratulate Dr. Shilling on his excellent paper. He has described in detail the type of inspection that has been

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in operation for a number of years and has proved so satisfactory in the inspection of aircraft material. The Inspectorate which Dr. Shilling represents squarely faces the fact that they cannot rigidly inspect everything and must rely to a large extent upon the fabricator. They place their trust in the fabricator, they check him, but most of the work is done by the fabricator, and that system seems to work very well.

I have no wish to cross swords with Messrs. Field and Salter, who represent a huge organization. Their paper is a very good one, and the only comment I have to make on the inspection aspect is that I do not believe one should have two separate inspection departments within one works. I believe that inspection should be of a positive and not of a negative character; it should take part in production, it should advise the production side, but it should not be under the control of production. The firm which I represent has one inspection department, which is based on the A.I.D. Inspectorate; over and above that a statistical quality control is applied during processing, the results of which are presented to the production personnel at the production meeting each week. Each week also results of the final inspection for the previous week are given in detail: the amount inspected, the amount rejected, the reason for the rejection. Trends are shown under various headings, and the production staff are thus given a warning of the possibility of any trouble.

I would agree with the previous speaker that the A.I.D. inspection is reasonably straightforward because of the specification to which one works and the fact that one can argue with the customer that the product conforms to specification. There are limitations, of course, in regard to such matters as the surface condition of sheets or bars, so that even with aircraft materials made according to specification, a regular exchange of views with the customer is absolutely essential, because from customer to customer there are differences in requirements.

On the commercial side, the position is rather different. Many customers order material to produce a certain product, and it is of no use arguing that it conforms to specification if it does not do the job.

There are inspectorates other than the A.I.D. who send inspectors round and who maintain that they are inspecting materials. Of course, they rely upon the fact that the fabricator is carrying out the rigid requirements demanded by the A.I.D. system of inspection.

I conclude by reiterating that inspectors should be completely independent of production, and that the inspection should be positive rather than negative. It should not take the form of a team of men at the end of the production line who simply throw out material. The job is not to reject material, but to make certain that the material that goes to the customer is useable and suitable for the end-product. Otherwise, quantity production of fabricated parts just cannot be maintained on an economical basis.

Mr. T. W. BUSHELL,* F.I.M. (Member): Unfortunately quality is a word all too rarely heard these days, and one is tempted to think of it as something continually being sacrificed on the altar of economics and commercial possibility.

Dr. Shilling has raised a number of points of importance to all concerned with ensuring a high quality of product in the metallurgical field. Such a point appears on p. 193, where it is stated that "one technically qualified member of the staff, who is not directly responsible for output, must be appointed". The operative words are "who is not directly responsible for output". It seems essential that this should be a general rule as far as works inspection staff is concerned, so that decisions on border-line cases may be made clearly in the light of experience and without any considerations of tonnage, output, or financial implications. The question to be answered in all inspection is: "Will this part perform the service for which it is intended?" And on that basis alone the decision should be made. It is of equal

importance, of course, to ensure that the person who is to supply the answer is capable of doing so.

There is at the present time, unfortunately, one school of thought which holds that if there is not some incidence of failure, then design is not economic. There is a second which believes that progress can be ensured only if there is an occasional disaster. Both are pernicious doctrines which appear to have been born of the urge for so-called economic efficiency, particularly when applied to the world of metals.

On p. 194 Dr. Shilling refers to certain alloys which have been described as "treacherous", but which, he says, might be more correctly described as "fastidious". There is much to be said for this point of view, particularly in the case of those alloys where the effective range of heat-treatment is very narrow, but might it not be said that all metals, while not necessarily being branded as treacherous, do include in all the "families" certain "individuals" that might well be described as "unreliable"? While this, again, could be said to be the fault not of the metal itself but rather of the people who melt it, the fact remains that whatever the cause, certain idiosyncrasies are present, many of which, if not altogether unknown to the designer, all too often are not appreciated by him. The control of quality then becomes even more important than is sometimes realized, and the papers submitted in this Symposium should be a source of considerable satisfaction, not only to the members of the Institute responsible for production, but also to those with a main interest as users of the materials in question.

From the point of view of the independent inspection organizations, too, there will be satisfaction in knowing to what an extent control of the manufacturing processes and the various items of works inspection has developed. Nevertheless, the limitations of all forms of testing and inspection must be kept constantly in mind, particularly where parts are of such a nature that some form of what has become known as "quality control" has to be used in the inspection departments.

While admitting the general excellence of the papers submitted and the care which appears to be exercised in the concerns with which the authors are connected, there are a number of points upon which explanation or clarification might be sought. On p. 202 of their paper Mr. Field and Mr. Salter describe the process of sheet stretching or stretcher-levelling. It would be interesting if the authors would indicate what effects, if any, this process has on any of the physical properties of the material so treated. In the case of the ferrous metals, it is known that gradual recovery takes place after such operations as reeling or straightening, and one assumes that in the case of the non-ferrous metals and alloys dealt with, similar recovery is possible.

On p. 207, Table I gives furnace and metal temperatures used in annealing, and it is noted that in each case there is a considerable difference between the two. As most of the alloys included are of the type where the heat-treatment temperature range is rather narrow, is it correct to assume that the metal temperature is determined by some form of contact pyrometer? In the case of the ferrous alloys, where most of the temperatures of heat-treatment are such that they are discernible to the eye, an experienced operator is able to estimate fairly accurately both when the temperature is attained and when it is uniform, but with all the light alloys this is not possible, so that information on this particular aspect would be welcomed. Is it possible for Mr. Field and Mr. Salter to indicate the actual difference in physical properties between the half-hard and quarter-hard conditions of the four alloys listed in Table II (p. 208), particularly in the case of the first two, where the difference in the "desired temperature for the metal" is only 5° C. between half- and quarter-hard?

Some very difficult heat-treatment and production problems are described on p. 210, and this applies particularly to the last paragraph of Section 2. As under these conditions it

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would appear possible for the hardness to vary considerably from sheet to sheet, is any check made on this figure after the flattening operation?

It is interesting to note on p. 216 that electronic testing has been instituted in the case of tubes produced by the port-hole type of extrusion dies. In view of the fact that in certain circumstances the extrusion effect, even on the solid sections, can extend for a considerable distance along the bars, has this method of testing been applied to such sections when they are intended for important structural members?

In view of the fact that quality does appear to be the first consideration in this field, it is interesting to read on p. 216, Section 3, that: "Method (a) is to be preferred to method (b) on the score of economy, but is suitable only for medium-strength alloys." One assumes that in such a case a change of procedure would not be instituted purely on the grounds of economy if an inferior product resulted, and more information on this point would be welcomed.

In discussing the heat-treatment of the alloys B.S. L.64 and L.65 as used for aircraft construction (p. 217), it is noted that the tolerance on temperature again is only of the order of $\pm 5^\circ \text{C}$., and it would be interesting to hear exactly by what means such a temperature deviation can be maintained. Must one assume from the following paragraph that the metal temperature is judged solely from the air temperature? This would appear to be so, but if, in fact, the charge temperature must be checked (although it is stated that "normally this is unnecessary"), how would this be done?

As is well known, some difficult machining problems arise when dealing with extruded bars. Could some indication be given as to whether the distortion occurring during heat-treatment also is greater in extruded than in rolled bars and sections?

In Mr. Miller's paper, the economic aspects creep in again on p. 223, where it is stated: "The virtues of some of these processes have been reported on... and there seems little doubt that they will be used to an increasing extent in the drive for higher-quality products. The only disadvantage is the increased cost." It must be recognized by designers and users alike that where circumstances dictate that products of higher quality than those currently available are to be used, increased first cost must be faced. Almost invariably, however, it will be found that the overall cost following such a change will be less because of better service performance, resulting in longer operating periods, with fewer shut-down intervals for repairs and replacements.

The same theme is evident on p. 235 of the paper of Mr. Hysel and Mr. Collier, where the old and new methods for annealing copper tubes are discussed, and one feels again that in certain circumstances such a change in production methods, while giving an article apparently cheaper as judged by first cost, can in the long run prove considerably more expensive to a fabricator or ultimate user.

The remarks on p. 241 regarding the straightening of wire, and the figures given in Table VI, are very interesting, as is the explanation of the marked difference in physical properties, particularly ductility. Is there any evidence to support this?

The unusual type of internal defect referred to at the bottom of p. 243 is not, of course, confined to the certain types of copper alloy mentioned. This is a defect with which the makers of steel wire have been troubled for a long time.

The paper by Mr. Edmunds and Mr. Lloyd is particularly interesting, but in spite of the obvious care and the considerable knowledge and experience brought to bear in the making of drop-forgings, one ends up with a feeling of uncertainty about the soundness and the physical condition of some of the items dealt with. No doubt the authors will reassure us on the efficiency of the subsequent checking.

This paper, in particular, emphasizes the need for the utmost vigilance in all operations concerned with the manufacture

of non-ferrous materials, and it would appear that the amount of time and money spent at the inspection stage is not by any means a luxury, but a necessity.

It must be remembered, however, that investigation of many failures indicates that in only a small minority of cases can the primary cause be traced to the metal itself; by far the greater proportion are due to faults in design or to the methods of fabrication or workmanship, and one is left finally with the feeling that if the same thought and care were given to these chapters in the creation of machines and structures as in the making of the metal itself, the number of failures encountered in practice might be very considerably reduced.

Dr. E. A. BLOCH* (Member): Control of quality becomes more important as the output of a product is increased, as better methods and better techniques are developed, as new applications are found, and—last but not least—as more stringent demands are made by the customers.

Switzerland has always been known as a country the quality of whose products is maintained at a high level, and the work of the Schweizerische Normenvereinigung is well known. The very complete statements made by the authors of the papers in this Symposium concerning the production of wrought non-ferrous metals and testing methods prove the existence of high standards of quality in England; so high, even by Swiss standards, that I shall have some difficulty in adding anything new to what has already been said. I shall therefore limit my remarks to the subject of non-destructive testing, and mainly to ultrasonic methods.

Aluminium-Industrie A.G. has recently gained more experience in this field, particularly in the inspection of semi-continuously cast extrusion billets. We were stimulated to extend ultrasonic testing in this field by some difficulties encountered in the fabrication of extrusions in 75S-type alloy for the Swiss aircraft industry. The qualities asked for were very high, and the extrusions were tested by the aircraft manufacturers by means of ultrasonic equipment. We therefore decided to utilize it ourselves to a greater extent.

Since ultrasonic testing is more easily applied to material in the as-cast condition and with bigger sections and simpler shapes, we decided to examine the billets before extrusion. Moreover, the rejection of defective products at this stage of fabrication avoids expensive work on faulty material.

A Kraut-Krämer instrument working on the reflection principle was utilized. All testing was carried out on billets cut to length for the ultimate extrusion operation, and ultrasonic waves were applied in the direction of the axis of the billet. With the assistance of the highly experienced aircraft inspectors, we were finally able to detect faults, such as cracks, inclusions, large-scale segregations, porosity, &c. To check what had been found by ultrasonic inspection, some of the billets were sectioned at the spot where the instrument had indicated the presence of faults. An exact correspondence of results was obtained.

Ultrasonic inspection gives perhaps too many details about faults in semi-continuously cast billets. We have detected by this method even microporosity, which certainly does not affect the quality of the extruded product. It will therefore be necessary to gain further experience about the importance of the indications that this method is capable of yielding.

Ultrasonic testing is capable of being developed into an automatic operation. In the United States such instruments have been designed, in particular an automatic precision instrument, using a water tank in which the billet is immersed and then automatically scanned by a probe which follows predetermined lines. Since the probe does not touch the billet, there is much less danger of its being damaged. Therefore the quartz crystal in the probe can be made thinner, and it is possible to apply ultrasonic waves of a higher frequency. Moreover, this permits the detection of faults in a much thinner layer of the surface of the billet. If the information supplied

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by the maker is correct, faults even at a depth of $\frac{1}{8}$ in. from the surface can be detected.

Finally, I should like to ask a few questions. In Dr. Shilling's paper (p. 196) it is stated that in the determination of proof stress of aluminium-clad aluminium alloys, two lines of proportionality can be observed in the stress/strain diagram. I should much appreciate some explanation of those two lines. Mr. Field and Mr. Salter (p. 216) refer to an electronic instrument with which tubes can be tested for soundness throughout their length. I should be grateful for some indication as to the kind of instrument.

Mr. K. E. THOMPSON,* B.Sc., A.I.M. (Member): All the papers under discussion, and also the contributions of Dr. Bloch and Mr. Martin, confirm that the use of non-destructive tests is growing in momentum, and the effect of this should be to increase the quality and consistency of products.

The ultrasonic method, which uses a pulse-echo technique, is well established for crack detection and has given a high degree of satisfaction. Greater demands are now being made on ultrasonics, however, for the detection of flaws, such as non-metallic inclusions, porosity, and coarse intermetallic constituents.

Dr. Shilling has indicated that it is important for control and inspection to keep pace with other developments. However, in the field of non-destructive testing for flaws, there is a lack of balance which needs rectification, since instruments and techniques available have been outpaced by the demands made upon them.

The two-probe technique is considered preferable for the examination of relatively rough surfaces, and is therefore used for as-cast extrusion billets and rolling ingots. It may also be employed for the examination of extruded sections, but its use is normally confined to relatively simple shapes. The single-probe technique, on the other hand, is more convenient in operation and can be used for examining a larger range of extruded sections than the double-probe method.

There are, however, a number of disadvantages with both these methods which make interpretation of results difficult:

(1) It is not always possible to distinguish between a cluster of small holes strategically placed and a major defect.

(2) Certain undesirable discontinuities do not necessarily constitute an ultrasonic discontinuity, e.g. the presence of sub-surface oxide skin in extruded sections may not necessarily be detected by ultrasonic methods.

(3) It is difficult to measure the size of a defect ultrasonically with no knowledge of its orientation or configuration. When examining extruded sections in chromium-bearing aluminium alloys, coarse chromium constituents are sometimes encountered, and subsequent examination shows them to be associated with porosity. The question has been raised, however, whether such constituents not associated with porosity would be detected ultrasonically.

(4) These methods do not readily lend themselves to the examination of complicated extruded shapes, and this is particularly true of the double-probe technique. Furthermore, difficulties can arise even with regular shapes, e.g. the examination of extruded rounds with a diameter of less than 4 in.

(5) Oil is usually employed to facilitate the ultrasonic coupling between the probe and the surface of the material under examination, but it is sometimes difficult to maintain a uniform film of oil under the probe, and a uniform coupling is essential in order to obtain consistent results.

This coupling problem can be overcome, however, by the adoption of the immersion method, already mentioned by Dr. Bloch (p. 516). One way in which this can be carried out is to place the material to be examined, together with the probes, into a liquid, water or soluble oil being quite suitable. In this way a uniform column of liquid is maintained between the transducer and the material under examination. Using

this method, the adverse effect of rough surfaces is reduced, and furthermore the whole thickness of the material can be examined for defects. Since the probes are not in direct contact with the material under examination, automatic movement of the probes is facilitated, and so a larger range of extruded sections can be examined. Even though this does offer some advantages, the method is comparatively slow and laborious, and industry is still looking for quicker and more precise non-destructive tests.

A method which can be regarded as complementary to ultrasonics is that based on eddy currents. This has been used more widely in Germany than in this country for the evaluation of variations in hardness and in composition, and for flaw detection. The present papers confirm the use of this method for the examination of aluminium alloy tubes and nickel alloy bar.

I should be glad to learn if, when using enclosing coils, this method is restricted to the examination of round shapes (as the papers imply). If that is the case, what are the difficulties to be expected when examining other regular shapes such as squares and rectangles?

It is my impression that in this country eddy-current methods are primarily used for flaw detection, and it would be interesting to know whether a reliable method has been developed here for evaluating hardness variations in aluminium alloys.

Despite the present limitations, there is no doubt whatever of the value of ultrasonic testing, and although eddy-current testing is still very restricted in its application, these two methods together will form a very important part of the inspection programme.

However, anything that can be done to reduce or remove the limitations will facilitate the interpretation of results and will help us to make a more accurate assessment of the quality of our products.

Mr. F. KING,† A.I.M. (Member): The authors have given us a wealth of detail on the factors affecting the control of quality in the heat-treatment and finishing operations. Several of them have again made reference to the great importance of control in the early stages of fabrication. Whilst this is accepted, we must not lose sight of the fact that final operations are also responsible for a high percentage of the rejections experienced on final inspection. This can be illustrated by quoting a few figures taken from an analysis made of a year's inspection rejection reports for a sheet mill producing a wide variety of sheet and strip products.

Approximately 25% of the rejections for the period under consideration were for rolling defects such as buckles and dish; broken surface, handling damage, and various forms of stains were the next most frequent causes for rejection. Other defects, such as gauge, blisters, slivers, and test failures presenting comparatively minor problems, together comprised a total of less than 10% of all rejections. It has been stated that poor shape from the earlier stages of rolling can frequently be corrected during final operations. The converse is also true. It has been found, when using a lightly-loaded 4-high mill for temper-rolling, that fluctuations in oil pressure in the roll-balance system can cause flexing of the work rolls, with consequent change of roll camber, causing unpredictable changes in central or lateral slackness in the rolled product. If consistent shape is to be obtained, it is necessary to ensure that the roll-balance is maintained at a constant predetermined pressure.

Several of the authors report varying degrees of success in the application of temper-letting-down or temper-annealing treatments. It has been stated that the purpose of temper-annealing is to remove internal stress and to modify mechanical properties, and that it is an art complementary to that of temper-rolling. The application of temper-annealing is much wider than this. It provides an economic means for

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the production of intermediate tempers from mills primarily designed for strip rolling, giving very heavy rolling reductions. The advantages which can be claimed for temper-annealed sheet are bright finish, improved ductility, and, provided that rolling reductions before temper-annealing are suitably adjusted, improved formability. The disadvantages of temper-annealing are those of oil-staining and shape problems, which also increase with increase in rolling reductions before anneal. Earing is not normally changed by temper-annealing unless some recrystallization takes place. The earing level of temper-annealed sheet approximates to that of the hard-rolled condition before annealing. Temper-annealed sheets are usually dry and require more care in handling than the equivalent temper-rolled products.

Depending upon the thermal history and the amount of cold reduction before temper-annealing, the temperatures to be employed for this treatment may be limited to a range of $\pm 15^{\circ}\text{C}$. down to $\pm 2\frac{1}{2}^{\circ}\text{C}$. In the latter case the temperature range is similar to that required for good solution-treatment practice, and the precautions taken with heat-treatment loads would be equally applicable. Where it has been found impracticable to temper-anneal in batch-type furnaces, owing to lack of uniformity in temperature, air sheet heat-treatment furnaces with well-spaced suspended loads have proved of value. Materials which have a wide temper-annealing temperature range have been successfully treated in flash-anneal furnaces.

Mr. Miller has mentioned (p. 226) the difficulties experienced with the batch-type furnace for temper-anneal treatment of wire. We would suggest that an alternative solution may lie in the strand-type annealing furnace, speeds and temperatures being adjusted to meet individual requirements.

The stress-relief anneal treatment mentioned by Mr. Hysel and Mr. Collier (p. 238) for the treatment of medium-hard 5% tin bronze rolled plate, to ensure satisfactory machine-shop production, is rather different from the partial-anneal treatment used in the aluminium industry.

The problem of distortion of plate on machining has also been mentioned by Mr. Field and Mr. Salter, who recommend adequate stretching as an answer to this problem, a recommendation with which we are in full agreement. For most applications, plastic deformation of $\frac{3}{4}$ –1½%, by stretching, is sufficient to prevent undue distortion on machining.

Of the various methods employed for process annealing, the vacuum method referred to by Mr. Miller (p. 226) appears to be the most intriguing, and we should welcome any further information on this subject.

Reference has been made to the possibility of continuous annealing of aluminium and aluminium alloy strip, and the complications, such as joining of coils, have been mentioned. These are of a minor nature compared with the complications likely to be experienced in the handling of soft hot strip. Continuous annealing of strip has been practised in the copper and brass industry for more than a quarter of a century, and it would be of interest to hear how this industry has dealt with the problem.

In the papers on the copper and nickel alloys, very little has been said about the methods of control of quality in the pickling and cleaning operations. Some discussion on this subject would also be welcome.

In dealing with the heat-treatment of extruded and drawn products (p. 217), Mr. Field and Mr. Salter express doubts about whether or not the use of the vertical-type heat-treatment furnace is entirely justified. For the heat-treatment of tube there is very little doubt about the advantage to be gained from the use of vertical furnaces. When quenching from a horizontal furnace, there is a risk of air becoming trapped in the tube and causing the load to become buoyant, resulting either in inefficient quenching or in serious distortion. This risk can be minimized by vertical heat-treatment and quenching, and it has been found that for tubes less than 1 in. in dia. adequate straightening can be carried out after vertical heat-treatment by stretching. For larger sizes of tube, a drawing reduction of 5% after heat-treatment is all that is required. I think that the authors mention a figure

of 15%. Final treatment after solution-treatment requires careful control. Tests on tubes finished by different methods show that the distribution of residual stress resulting from these operations can make a great difference to fatigue values.

Mr. Miller states that, as an alternative to batch furnaces, salt-bath furnaces can be used for the solution-treatment of wire. These may be satisfactory for wire heat-treated in the strand form, but are undesirable for the heat-treatment of coils of wire on account of difficulty with the removal of salt after quenching. Unless an efficient means of removal is employed, possibly by re-winding, serious corrosion problems are likely to be encountered. The oxide film formed during salt-bath heat-treatment can be a source of heavy die wear on subsequent manipulation, such as drawing or rivet-making.

Contraction in volume in strip on annealing has been mentioned by Mr. Hysel and Mr. Collier, and also by a number of contributors to the discussion. Similar problems have been experienced on heat-treatment of aluminium alloys, and if rivet holes or similar holes are to be blanked into components before heat-treatment, allowances should be made for the changes in dimensions which are bound to occur.

Mr. Field and Mr. Salter, and Mr. Hysel and Mr. Collier, state that as long as steps are taken to keep the amount of residual oil to a minimum, freedom from burnt-oil stains is greatly assisted. We agree that the solution to many oil-staining problems lies in the development of improved techniques for oil removal before thermal treatment. A study of the chemistry of oil breakdown in service and during annealing is also important, and the methods used for the control of rolling and drawing lubricants is a subject coming within the scope of the present Symposium.

Turning to the importance of testing procedure, we would endorse Dr. Shilling's comment that tests called for in the specification do not always yield results of direct use to the designer. This is a fact which has not always been fully appreciated by consumers. Differences amounting to several tons per square inch in ultimate tensile stress may be experienced between test-pieces selected from the core and from near the surface of heavy extruded sections. The mechanical properties of thick plate follow quite a different pattern. Depending upon the amount of reduction from the cast ingot and upon the degree of recrystallization occurring on solution-treatment, the longitudinal properties at the core of plate can exceed those of the surface layers by as much as 2–3 tons/in.². To avoid the necessity for an excessive amount of mechanical testing, the aim of quality control should be to enable the mechanical properties in any location to be predicted with reasonable certainty from the results of a limited number of tests.

Hardness testing is a requirement of many specifications and serves a useful purpose in the detection of the more serious cases of lack of uniformity. However, as has been pointed out, in the case of aluminium alloys the correlation between hardness test and other mechanical properties is not very satisfactory and is subject to many limitations, quite apart from being time-consuming. The merits of alternative methods might well be discussed.

In reading through the papers, figures quoted for grain-size standards at first sight appear to be at variance with our own experience, but this may be accounted for by the fact that a different method of measurement has been employed. The same difficulty has been experienced with earing values, and it is thought that these two subjects should receive further consideration. Standards of flatness for sheet are another matter of importance if uniformity between suppliers is to be established, and it would be interesting to know whether anyone has been able to define various standards of flatness in precise terms.

The function of the metallurgist has not been mentioned in any of the present papers. Due tribute has been paid to the skill of mill operatives and to the part played by the inspection department, but it is the metallurgist who has the task of investigating consumers' requirements and the nature of the processes involved in fabrication and of applying this know-

ledge in such a way as to enable the production departments to exercise the maximum amount of flexibility in carrying out their operations. It is only by close liaison between the engineering, technical, and production departments that improved quality can be achieved. The present series of papers serves the useful purpose of indicating to all, some of the problems which have to be faced by these people from day to day.

Mr. R. T. THORLEY,* B.Sc. (Junior Member): I should like to support Mr. King's plea for standardization in the methods of measurement of the earing characteristics of aluminium alloy sheet, so that those concerned with the investigation and control of this property may be in a better position to exchange technical information. The value quoted for the earing properties of a given material is a function both of the pressing conditions and of the method of measurement. For example, earing is sometimes measured solely as the difference in height between the ears and the troughs, although a more common method is to express the difference in height between the ears and the troughs as a percentage of some arbitrary quantity, such as the height of the troughs, the ears, or the mean of the two. These methods give, of course, vastly different results, and the values are, moreover, very dependent on the pressing conditions, such as punch-and-die combination and blank diameter.

For instance, using a Swift sub-press with a punch dia. of 2 in. on a standard material, values varying from 1.5 to 5.3 mm., or 8.2 to 16.9%, were obtained merely by altering the blank dia. from 3 to 3.75 in. These differences may, however, be much reduced by the use of a modified formula on a fully drawn cup, namely:

$$E^0 = 100 \frac{h_1 - h_2}{h_2 - k}$$

where h_1 is the height of the ears, h_2 the height of the troughs and k is a constant. For each tool combination k is best determined experimentally, but satisfactory results have been obtained by the use of an empirical formula involving punch and die diameters and profile radii, blank diameter, and metal thickness. For experimental determination of k , cups are pressed from a number of blanks of various diameters, using standard material; h_1 is plotted against h_2 , and the point at which this line intersects $h_1 = h_2$ gives k .

This method provides satisfactory agreement between different sets of tools so long as ironing of the walls or the tips of the ears does not take place. As an example of its operation, the results shown in Table A may be quoted. They refer to tests carried out with a wide range of pressing tools on three materials of different earing characteristics. The results

are quoted using the $100 \frac{h_1 - h_2}{h_2}$ formula and the alterna-

tive now proposed. From a comparison of the coefficients of variation, the superiority of the new method is obvious.

TABLE A

$\frac{h_1 - h_2}{h_2} (100)$		$\frac{h_1 - h_2}{h_2 - k} (100)$	
Mean Earing, %	Coefficient of Variation, %	Mean Earing, New Units	Coefficient of Variation, %
16.04	26.8	32.16 ^e	2.0
7.78	16.7	15.70 ^e	4.6
2.70	24.4	4.92 ^e	13.3

In the paper by Mr. Field and Mr. Salter, the comment is made that a low-silicon, high-iron content is conducive to a fine grain-size in commercial-purity aluminium or in the 14% manganese alloy. Whilst it is agreed that an increase in

iron tends towards a fine grain-size, do the authors imply that a low silicon content is necessary from this point of view? Our own experience is that silicon between 0.2 and 0.5% has very little effect on grain-size. In fact, a statistical analysis on the 14% manganese alloy has shown high silicon to give a slight grain refinement. Perhaps the authors would like to comment further on this.

I have not found any mention in the paper by Mr. Edmunds and Mr. Lloyd of one forging defect which can be very troublesome. It occurs mostly in large forgings of the D.T.D. 683 type and, since it is most noticeable when present in the flash area, we have termed it the "flash-line" defect. Its presence may be detected by ultrasonic inspection, since it is aligned in the direction of the grain flow in the flash line. If a piece cut from this area is fractured, the defects show up as shiny facets (see Fig. F, Plate LXXXVI). The particular defect illustrated is a very large one, its length being about 1 in. It results in a considerable decrease in the strength across the flash.

Little information has been published on this subject, and any observations would be welcomed. We suggest that the defect is due to the presence of films of oxide in the flash. These films are very thin, but may consist of several layers. Fig. G (Plate LXXXVI) shows a single-layer oxide film ($\times 1500$). Since these films are flat plates, failure along them would result in a fracture surface with a number of flat facets and consequently a shiny appearance. In the case of forgings made from extruded stock, these films could be introduced from the periphery of the extruded billet, the flow in some forgings causing the peripheral zone of the extrusion, and hence the oxide films, to occur in the flash and in the flash line. Consequently the flash-line defect should be eliminated, or at least reduced, by very heavy scalping of the extruded stock.

Such films may originate, in part, from the well-known sub-surface defects sometimes found in large-diameter extrusions as a result of the flow of oxide from the container and the periphery of the billet, but it is believed that they may be aggravated by the presence of defects in the surface layers of very large-diameter continuously cast billets, which penetrate to a far greater depth than is generally known. Very large forgings may sometimes contain defects of a somewhat similar type in the body of the forging. These also may originate from the cast stock, but they could not, of course, be eliminated by heavy scalping.

Mr. P. C. MURPHY,† B.Sc., A.I.M. (Member): Reference has been made to abnormal grain growth in aluminium wires on drawing a large amount. This, I think, may be regarded as an ordinary example of secondary recrystallization. It is well known that if grain-size is plotted against cold work, at very small amounts of cold work there is a rise in grain-size on annealing. What is perhaps not so commonly realized is that with high degrees of cold work, usually about 90%, there is a further peak in the grain-size curve. It has been found that, depending on thermal history, preheating, and other factors, this peak can be pushed back in some alloys to about 30%, so that it is not surprising that rather unusual results are occasionally obtained. The reason for this is still controversial. One of the most important factors is, of course, the well-known dispersed phase, but explanations based on this alone cannot account for all the phenomena, and possibly the most that can be said is that a combination of orientation relationships and dispersed phases is responsible.

Mr. Field and Mr. Salter describe (p. 207) a method of measuring grain-size in which the roughness of the dome produced in the Erichsen indentation test is compared with a series of arbitrary standards. The method takes into account any variation in grain-size which occurs throughout the sheet thickness, and it will show up "ghost" structures. By revealing "orange peel" it can assess what pressing and spinning people mean by "grain." The method is adequate

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for commercial-purity and 1½% manganese alloy sheet in gauges from 0.125 to 0.015 in. Above 0.125 in., grain-size can be similarly assessed by the appearance of a 180° bend over a minimum radius. Below 0.015 in., especially on tempered sheet, it is advisable to supplement the test by a macro-etch of the surface.

Standard domes covering a wide range of grain-sizes can be conveniently prepared in thoroughly homogenized 1½% manganese alloy which has been given a variety of cold reductions followed by different rates of heating to annealing temperature. Such arbitrary standards can be used for assessing "orange peel" on all alloys and tempers, but it will be appreciated that correlation with actual spatial grain-sizes is limited to alloys, gauges, and tempers approximately similar to those in which the standards are prepared.

All manufacturers and large users of aluminium alloys must have devised a system for standardizing grain-size measurement throughout their organization, but unfortunately there is no generally accepted method used in published work, and at times it is difficult to correlate various methods of expressing grain-size. Grain shape varies with both temper and alloy, and this precludes the general use of standard comparison charts.

The most complete method of specifying grain-size is by giving the actual—that is, the spatial—average dimension of grains in each of three dimensions, describing if necessary any changes through the section. In practice, the determination of these dimensions need not be particularly tedious. It can be shown statistically that 43% of the total number of grain-sizes in an aggregate will have a planar (as measured on the microscopic section) grain-size of at least 90% of the spatial grain-size. By intelligently measuring 10 of the larger grains along three axes, reproducible results on spatial grain-size can be obtained. Should many such determinations have to be made on comparable materials, standard photographic negatives of accurately determined grain-sizes can be placed alongside the microscopic image of the unknown and the magnification adjusted until a match is obtained.

I should also like to make some comments on the question of tubes. In their paper, Mr. Field and Mr. Salter (p. 215) refer to pits and cracks as defects encountered in tube-drawing, especially of strong alloys. These and similar defects can to a large extent be associated with the extruded bloom and its subsequent treatment. In the first instance it is essential that bloom should be extruded at least as carefully as section, and any cross-hatching, pick-up, or other defects rigorously avoided. The inner surface of the bloom must also be considered, and close attention given to the cleanliness and lubrication of any mandrels used. Scoring of the inner surface by the mandrel is often apparently removed on drawing, but may reappear as blisters on thermal treatment. At this stage careful handling is of great importance, and scores, traffic markings, and general damage must be avoided.

Most alloys require bloom annealing and, if furnace capacity and mill loading allow, it is advisable to carry out this operation under conditions different from those used for intermediate annealing, as it is found that as-extruded bloom requires a substantially higher annealing temperature for adequate softening. The use of this higher temperature carries the penalty that relatively slow cooling rates are required with most heat-treatable alloys.

The optimum annealing conditions for maximum softening may not always be desirable from other points of view. This is exemplified by the aluminium-magnesium alloys, which certainly anneal more completely at a high temperature, but in so doing acquire a thickened oxide coating which offsets the advantage of the increased softness. Even after bloom anneal at high temperature, full softening cannot be induced in the absence of cold work. This must be taken into account when planning drafting schedules for strong alloys, in which cracks will develop if heavy reductions are attempted before inter-annealing.

Annealing represents another point where the tube is particularly susceptible to damage, and unless the utmost care is taken in the loading and unloading of annealing skips, transverse scores will occur. These are especially detrimental to strong alloys and will result in rejection for cracking on inspection of the finished tube.

In the production of tubes in commercial-purity aluminium and the 1½% manganese alloy, particular care must be taken with the control of grain-size. These alloys are not bloom annealed, and a bloom size which allows adequate reduction before any intermediate anneal must be chosen. The billets used in the extrusion of the 1½% manganese alloy bloom must be given a high-temperature preheat comparable with that used for sheet ingots.

The production of shaped tubing, such as sharp-angled box section, calls for especial care in planning, particularly if heat-treatment is to follow the shaping pass. The material must be soft enough to fill the shaped die completely, but must emerge with enough cold work to be immune from abnormal growth on heat-treatment.

The viscous compounded mineral oil mentioned as being suitable for tube- and wire-drawing is undoubtedly a most effective lubricant for general use. It can be replaced with advantage in certain applications by a spirit-dissolved wax, which is applied by immersing the tube, draining it, and allowing it to dry before drawing. The tube can then be drawn in several passes without further application of lubricant to inner or outer surfaces, resulting in a considerably increased machine utilization.

As mentioned in the discussion of last year's Symposium, there is a definite need for an up-to-date appraisal of the techniques and problems of tube-drawing. This might result in the formation of guiding principles for what is still essentially an art rather than a science.

Professor Dr. Ing. A. VON ZEERLEDER* (Member): I am interested to find, from the paper by Mr. Field and Mr. Salter, that the molten lead bath is still employed, and I would like to know to what extent it is used in the British aluminium industry. I note also the statement by the same authors that the conveyor-type furnace to which they refer is higher in operating cost than the batch-oven type. In our experience the consumption of electric current is not greater, but it may be that the labour and capital costs are higher with this type of furnace. The annealing effect is improved by leaving the batch for an hour or more in the furnace so that it may cool down very slowly. In order to have the furnace ready quickly for the next batch, the load is sometimes taken out of the furnace, put on a platform, and covered with an electrically heated bell to provide slow cooling.

It is mentioned in the paper that the arbitrary Erichsen numbers correspond with certain grain counts. In our experience this correspondence is found only with pure aluminium. In aluminium alloys, particularly of the aluminium-magnesium-silicon type, the grain is always much coarser.

It has been pointed out by Dr. Bramley that it is almost impossible to avoid copper dust falling on aluminium in plants where both aluminium and copper rod are rolled. We recommend, in cases where this cannot be avoided, that the aluminium rod be cleaned by pickling it in nitric acid solution of at least 20% strength, in order to avoid corrosion of the aluminium. To make sure that the pickling is fully effective, it is important that the copper nitrate concentration in the solution be kept down; otherwise, there will be cementation of copper on the aluminium wire. Fortunately, we understand that the simultaneous rolling of copper and aluminium rod is no longer practised, so that this problem ceases to be very important.

Mr. R. C. ANSELL†: Mr. Field and Mr. Salter mention that it is customary to interleave sheets with tissue paper during

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packing. It is worthwhile considering in some detail the tissue paper used, as the cost is something like $\frac{1}{2}$ d./yd.², and in addition there is the fact that it can give rise to corrosion problems under certain conditions during transit or storage. In the course of manufacture the paper, whether chemically or mechanically digested, is always thoroughly washed with water, and its characteristics will be determined by the dissolved solids in the water remaining in the processed paper. Trace amounts of such impurities as chloride or sulphate are dangerous from the corrosion point of view, since ordinary paper contains approximately 10% of water by weight and will readily absorb further quantities, giving rise to the conditions for typical paper-corrosion patterns to be produced on the sheets in contact with it.

There are several ways in which this form of corrosion can be overcome. It is possible to control the acidity and chloride content of the paper purchased, and for domestic use it has been suggested that an acidity not greater than 0.01%, calculated as sulphuric acid, and a chloride content of 0.25%, calculated as sodium chloride, should be stipulated. For exported material, however, especially where greater humidities may be encountered, higher-quality paper must be used with an impurity level less than half that just mentioned. Alternatively the tissue papers can be treated with a corrosion inhibitor such as sodium benzoate or sodium chromate, both of which can be extremely effective, but which further increase the cost by approximately 50%.

In Dr. Shilling's paper (p. 198), there is a reference to thick plate used for complex machinings and to a porosity defect which can be detected after machining. The term "porosity" is not strictly accurate in this case; the defect is not evident in the as-cast structure but appears after preheating. It is thought that the cavities are produced by gas, retained in solid solution during casting, diffusing to the grain boundaries and passing into the areas where intermetallic constituents are being taken into solution. The cavities will remain unless the reduction in area is greater than 85–90%, or unless the melt is thoroughly degassed before casting. After casting, and before hot rolling, a slice is cut from each ingot, which is preheated, faced, and treated with a penetrant dye, used in conjunction with a developer solution.

Owing to the small size of the holes, it has been found necessary to increase the sensitivity of the test by using a warm specimen and allowing the dye to remain on the surface for approximately 30 min. before washing off the coating and spraying with the developer. If the specimens are examined immediately after spraying, then the sensitivity is greater than with the Bengough-Stuart anodizing process. The plate is examined after heat-treatment in the manner described, or by the Bengough-Stuart anodizing process, but it will be appreciated that this form of testing is restricted to one particular portion of the plate, and that to test the material comprehensively such methods as ultrasonic inspection must be employed. A technique for this has now been developed, using standard equipment, notwithstanding the difficulties in interpretation which limit the application of the method. It is hoped that some of these difficulties will be overcome by using an immersion technique.

A further point is the statement on p. 210 of the paper by Mr. Field and Mr. Salter that 520° C. is the maximum safe working temperature for nitrate salt baths. It is common practice in the industry to operate baths at 535–540° C. for considerable periods without any signs of trouble. I wonder whether any other producers can offer comments on this subject.

Mr. N. I. BOND-WILLIAMS,* B.Sc. (Member of Council): In the first place, although it may appear a heresy to inspectors, I feel strongly that the segregation of an inspection function into a water-tight compartment, quite separate from production and processing, is an organizational fallacy, and one which we should not accept simply because the inspectors

tell us that it is a good idea. As we perfect controls in our industry, both in equipment and in methods, so the people who operate the machinery and supervise the processes have less and less to do except to look after quality, and eventually, if development continues in the direction which I believe it to be taking, we shall find that direct workers do nothing but control quality, and that everything else will be done almost automatically.

Psychologically, I think that it is a great mistake to dream of divorcing quality from the duties of the workman. I have heard it said that workmen are less conscious of quality than they used to be, and that they do not make such good stuff as they used to make. That is not surprising, if we take that function away from them and give it to a man in a white coat. I agree, however, that it is necessary to have an umpire who can say at the end whether something is right or wrong, and, if it is wrong too often, we know what to do about it.

I should like to refer to the question of dimensions. Mr. Smith deplored the lack of detailed discussion of tooling, tool materials, and the accuracy of tools. The developments in which Dr. Messner is interested in Switzerland, and which many of us have seen, show that a very great deal of the quality for which we call in our ultimate product can be controlled by good tool-room work and by the application of good tool-room methods.

In these papers very little is included about dimensions, and undoubtedly close control is very hard to attain. It is particularly difficult to measure, and therefore to regulate, the dimensions of soft materials. A good many of the

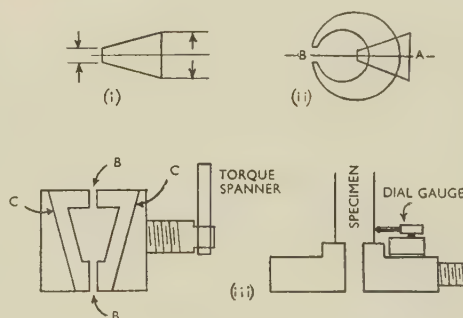


FIG. H.—Illustrating Development of Pressure-Type Precision Measuring Gauge. (Bond-Williams.)

A—Specimen.
BB—Checking point for thickness measurement.
CC—Reference surfaces for contour measurement.

materials under discussion are soft; certainly they are generally softer than the instruments employed for measurement. On considering our systems of measurement, it appears that we usually employ something like a small power press, with very hard surfaces, which is applied to the dimension to be measured, and we hope that by reading the dial we shall get the right answer.

Let us take as a very simple example the product to which Mr. Hysel and Mr. Collier refer quite frequently, and see into how much difficulty that leads us.

Fig. H (i) is an exaggerated drawing of a commutator section, made usually of hard-drawn copper. It is almost impossible to measure the two most important dimensions by any method utilizing the pressure type of gauge to which I refer. The edges come to a sharp point, and the application of a micrometer there will not work, for obvious reasons.

That leads to a consideration of the general problem of making such measurements, and possibly some experience which we have had may be helpful in arriving at a solution to similar problems, with different and perhaps more com-

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plicated sections. I shall omit reference to the chain of experiments which led to the result, but ultimately the solution of our problem was found to be to build the specimen, as it were, into the gauge and then measure something else with it. We take a gauge with conventional measuring anvils at *B* (see Fig. H (ii)), and the specimen which it is wished to measure is built in at *A*, the measurement being made at *B* with steel slip gauges. The surface to be measured is thus made much larger, and therefore less likely to suffer distortion, than if checked between the rather small anvils, applying considerable local intensity of pressure to the material. This leads to a type of gauge (Fig. H (iii)) in which the specimen is held between jaws similar to those of a vice, closed under constant pressure, and subsequently the contour of the specimen is traced with the aid of delicate dial-gauge instruments, in addition to the checking with slip gauges of the gap between the vice jaws themselves.

That is one solution of this problem of measurement. I quote it because I think that the problems of measurement have been avoided a little in this Symposium. As metallurgists, and certainly as production metallurgists, we cannot expect to control the whole of our processes if we evade one particular item which seems to be of special importance. I am sure that Mr. Kayser will agree with me on this, that although amongst all the factors in mass production this seems to be the greatest, we say the least about it. I would therefore encourage metallurgists to take a greater interest in the problems of dimensional accuracy, and particularly in solving some of the problems of measurement seldom tackled by production engineers, except in relation to hard materials, which do not present the same difficulties.

Mr. BENGT STRÖM* (Member): I should like to make two comments on Mr. Miller's paper. One is concerned with the use of the vacuum furnace. For about six months a set of these furnaces has been installed at one of our works. They have not been in operation long enough for us to form a judgement, but while the critical temperature of sticking is increased by perhaps 50° C. at a pressure of a few mm. Hg, it is not eliminated. This 50° C. is, of course, very important when annealing fine-gauge copper wire. One of the drawbacks of the furnace is the lack of convection during the cooling cycle, which therefore is very long, and a greater number of bells are needed.

My other comment is on the importance of the temperature of recrystallization of copper wire. One of the electrical companies in Sweden asked us to provide copper wire for enamelling purposes with a specified maximum recrystallization temperature. We discussed this with the copper suppliers in Sweden, and after investigation they finally adopted a routine test so they could check the recrystallization temperature for each batch of metal and could get a result which corresponded to the recrystallization temperature of the final wire (<1 mm. dia.). Based on the Smart and Smith method for determining the recrystallization temperature, 1 hr. at 210° C. has now been specified as the maximum recrystallization temperature for copper to be used for enamelled wire.

Mr. ALLAN F. NORRÖ (Member) †: Mr. Miller refers on p. 224 to the work of Smart and Smith on softening temperatures. Every charge of copper made at our works is tested for softening temperature in accordance with the methods of Smart and Smith, and we have an arrangement with our biggest customer that if the softening temperature is higher than 210° C., a special note is made of it.

Mr. Miller states that none of the commercial varieties of copper has a softening temperature below 200° C. I am proud to report that we have often achieved a temperature of 190° C.

I should like to hear the reactions of those taking part in

the Symposium to the following. If, owing to the difficulties arising from springiness in annealed wire, a special specification for softening temperature in wire, of say 210° C., were to be introduced, what would people in England think of that idea?

Mr. R. D. WEBER‡: As a production man concerned with the manufacture and quality control of copper rod and drawn copper products, I should like to make a few comments on Mr. Miller's paper. I am particularly interested in the annealing of drawn copper sections and drawn copper strip. Mr. Miller says on p. 227: "It is significant that welding is never experienced when using steam-atmosphere bright-annealing furnaces." I must confess that it can be done! It happened in the case of strip less than $\frac{1}{16}$ in. thick, which was annealed at a very high temperature. Apart from that, we have been successful in steam-annealing strip at temperatures up to 650° C.

On the question of vacuum-annealing furnaces, I have discussed the matter with some colleagues from Germany who are of the opinion that the operation of such furnaces is generally cheaper than that of controlled-atmosphere furnaces. I do not know whether that has anything to do with the difference in price of electric power on the Continent and in this country. I am not quite sure whether the hoods and bells have to be made heavier, or whether a form of corrugated hood could be used.

My firm is now quite successful in producing commutator segments. I agree with Mr. Bond-Williams that the tool-room aspect is of great importance. We can produce accurate material well within tight specifications by paying special attention to our dies.

Mr. R. E. BERRY,§ M.Eng., A.I.M. (Member): I should like to give a word of warning about heat-treatments carried out solely to make material comply with specification. In this connection I would refer to p. 237, where Mr. Hysel and Mr. Collier deal with the heat-treatment of complex aluminium bronzes. In that case alloys are involved with which some members may not be familiar. D.T.D. 197A is a copper-base alloy with approximately aluminium 10, nickel 5, and iron 5%. In a great many instances these alloys are used for fatigue- and creep-resistance applications. They can be heat-treated, but, during heat-treatment to improve their mechanical properties, precipitation of nickel and aluminium compounds often occurs. The warning I would give is that whilst it is possible to enhance the mechanical properties of the alloys and bring them within the specification limits, one is liable to upset the fatigue and creep properties by so doing.

I should not like anyone to think that it is always or even usually necessary to heat-treat extruded or hot-rolled bars of D.T.D. 197A alloy to get the required mechanical properties. In our experience it is the exception rather than the rule to carry out any heat-treatment at all on this alloy. It is perhaps rather beyond the scope of this discussion to refer to the contents of Table V (p. 237), but I am astonished at some of the values which Mr. Hysel and Mr. Collier have obtained. No doubt these are test values, but, to take one case, a figure of 15% elongation for the extruded material is unusually low. Perhaps the authors could check this.

Dr. O. H. C. MESSNER|| (Member): The methods of quality control in general, and in particular in heat-treatment and final operations, have become so effective in the past few years that it is possible not only to exercise effective control but also to turn out a product far superior to that which has hitherto been considered standard. Opinion varies greatly as to whether the non-ferrous metal industry should adhere to the standards previously established and charge the

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customer heavily for any product the quality requirements of which are in excess of such standards; or whether the new methods should be regarded as improved tools, which enable a superior product to be supplied to the benefit of the customer and to the ultimate benefit of the manufacturer in providing new fields of application of metals.

A tendency undoubtedly exists for the non-ferrous metal industry to deal in more or less "tailor-made" goods, in contrast to the iron and steel industry, whose products are mostly of a standardized nature. In Switzerland, and more particularly in some of the firms with which I am associated—the Fonderie Boillat S.A., Reconvilier, and the Metal Works, Ltd., Dornach—the opinion is held that, above all, the demands of the market should be met and the quality of the product improved to the greatest possible extent. We have noted an increasing tendency for special sizes to be required, e.g. strip instead of standard sheet.

Another important question which arises is whether, particularly in the final operations, quality control should be entrusted to the operatives, or whether special staff should be appointed for this task alone. We have found that better results are obtained if certain means of quality control, e.g. continuous strip gauges, are put into the hands of the operative, and he is made responsible for the quality of the product. The laboratory staff simply check the finished material and advise the management what has been produced. The tendency in the U.S.A. is to create a very sharp distinction between metallurgical control and production, and at all levels to hold the works personnel responsible for output alone, while the metallurgical control supervises the quality of the product through every stage of manufacture.

In providing a "tailor-made" product we have found it essential to secure the fullest co-operation of the workmen, who are fully conversant with the properties which the goods must possess and how these can be attained, but we are, of course, working under very special conditions in producing high-quality specialized products.

Although instances of season-cracking in copper are very unusual, we have recently encountered what appear to be some cases in connection with copper tubing for water-supply purposes, having soldered joints, although there is a possibility that fatigue was responsible. Have any similar cases been met with in the British industry and is it customary to adopt the practice so well known for brass and to stress-relieve the material?

Pitting corrosion of copper tubes we have traced back to iron filings, or similar particles, which have rusted and thus become more noble than the surrounding material, or to carbonaceous residues. Cases are very rare, however, and in view of the widespread use of iron tubes with copper or brass fittings, the danger does not seem very serious. I wonder, however, whether any measures have been taken to control the surface quality of copper tubes, especially in respect of iron residues or, at a later stage, inorganic matter. This would be a costly procedure, but might avoid a great deal of subsequent trouble and expense.

Incomplete recrystallization of 63 : 37 brass tubes has been noted on several occasions. The tubes were annealed in a continuous roller-hearth furnace at a speed of 8 in./min. The length of the annealing zone of the furnace was of the order of 19 ft., and the annealing temperature between 520° and 580° C. The material had been previously cold-worked approximately 30%. Not only was the recrystallization incomplete, but also a certain amount of the unstable β constituent remained in the brass. To avoid this, the furnace had to be operated so slowly that it became inefficient. Is there any means of avoiding the trouble? Would the use of a muffle furnace be more satisfactory? If we continue to anneal in the normal way, it is necessary to make constant checks to ensure that complete recrystallization has taken place. To test for recrystallization as a routine operation presents considerable difficulties, and we should be glad to know whether any method has been devised of overcoming the problem.

It is becoming more and more usual to test spring material intended for electrical applications, particularly telephone installations. Conformity with the so-called *Federungsgrenze* (limit of springiness) laid down in the German specifications D.I.N. Nos 1777–1780, is sometimes required, but we have found that a determination of these values leads to very uncertain results. In our opinion, hardness tests, combined with bend and spring-back tests, should form a sufficient basis of assessment. How are such tests, especially of telephone contact springs, conducted in the English industry, what type of test is considered most suitable for non-ferrous springs, and what specifications are laid down by telephone manufacturers or other bodies?

Dr. SHILLING (*in reply*): Dr. Bloch, in his suggestion that ultrasonic testing should be used at the billet stage, omitted to mention a reason for its adoption that we consider very important, namely that some serious defects get squeezed up and compressed and are not responsive to ultrasonic testing in the extruded or forged state. On the other hand, it has also been pointed out that the reverse can occur.

Dr. Bloch asks whether he can be enlightened regarding the two proof-stress lines mentioned on p. 196 of the paper. In a clad material, two substances are involved—the cladding, which is very thin in proportion, and the main body—and there are two yield points. In carrying out the tensile test, the one yield point is reached first at which the straight-line effect of the cladding disappears, and a slight kink occurs in what might otherwise be a straight line.

The A.I.D. would put forward the view that proof-stress testing is affected by the accuracy and sensitivity of extensometers. We are finding that the more accurate and the more delicate the measurements, the greater becomes the doubt whether a straight line exists for any specimen that is being tested. However, the old method of proof-stress determination has given very valuable and reliable results in the past and obviously must remain in practical use, at any rate for some years to come.

Mr. Bradbury seems rather to suggest that if the A.I.D. insist on inspecting every stage of the process and, having done so, find that the manufacturer has carried out all parts to their satisfaction, they ought then to accept the final result whether it is good or not. I do not agree. We are not responsible for the process, but we are responsible for assessing the reliability of the products. It would not, however, be necessary to exert any pressure on a manufacturer to change his methods if, having carried out his process very carefully, he found it did not give him the required result.

There has been the further suggestion that we tend to be too meticulous regarding analytical work, but, here again, we are interested only in the final analysis, that is, in just what comprises the material that is going to be supplied to the customer. If there are ingredients which have gone into the product and ultimately change or even come out, this does not concern us except in so far as we are interested in the process.

It is true that some of the aeronautical specifications which Mr. Kayser particularly mentions appear to be a little wide, but there is a reason for this; if they were not so phrased, there would be thousands of specifications and not hundreds. Perhaps the point can be illustrated in the following way. A specification may state that the zinc or the magnesium content of an alloy shall lie between the limits 3% and 6% (fictitious figures, used purely for illustration), but it does not follow that any manufacturer, if he valued his products at all, would be happy to work within those wide limits on his normal manufacturing process. He would from experience find perhaps that 5.5% was best suited to his particular process and would control his limits to some such tolerance as 5.45–5.55%, or even more closely, depending on the importance of the element. If we discovered that a manufacturer had suddenly decided to change his tolerance limits, even though he had changed them to something still well within the specification, we should be very interested to know what had happened and why.

A few years ago it could be stated that non-destructive testing was divisible into two broad classes, namely radiology and the rest, meaning that radiology was well established and that the rest were, to some extent, unknown. Today I think we can put ultrasonic testing midway; of "the rest" it is certainly growing the fastest. Although, as the experiences quoted show, the answer is not yet quite certain, there is undoubtedly a very big future before it. I think that with more experience and more knowledge we shall be able to class ultrasonic testing in the same reliable field as radiology; the word "reliable" presupposes a knowledge of its limitations.

The "rest of the rest"—eddy-current methods, high-frequency bridge methods, and so on—have not grown up yet, but that does not mean that they will not do so, although we do not know which of them will develop. Take, for example, eddy-current methods. In trying to scan or inspect a rolled bar or other product having a regular cross-section by an eddy-current or a high-frequency bridge method, one is quite safe provided that it is known that nine out of a possible ten factors are absolutely invariable, so that the only variable factor is the one under investigation. It is obvious that this is not likely to happen very often. It is hoped to overcome such difficulties, because the method has great potential value.

Mr. Matthewson has anticipated a point which I should have raised with Mr. Field and Mr. Salter, namely the question of there being two different and separate inspection departments within one firm. Our general experience is that this is unusual. The A.I.D. prefer a firm's existing inspection staff to operate, for the simple reason that they are more likely to know their job, and we rely on people who know their job and do it.

In reply to Mr. Bond-Williams, it is the aim of the A.I.D. to base inspection as near to the job as possible while the work is in progress. To suggest that it should be kept in a water-tight compartment would be heresy to the A.I.D., and the reverse, which Mr. Bond-Williams suggests, is certainly not true.

The question of change of nomenclature raised by Dr. Bramley has already been discussed and was turned down by the Society of British Aircraft Constructors. The suggested use of the letter T, for example, was an attempt to conform with American practice. This practice itself has since been changed, and one has only to look at B.S. 1476 and compare it with Alcoa Temper Designations (January 1948) to realize how complex the situation has become. Any attempt at the moment to alter a system that has been in use in the aircraft industry for many years would create chaos.

Mr. SALTER (*in reply*): Dr. Shilling has referred to my Company's practice of having within its factories two inspection organizations, and indicates that he would be quite happy, if we were contented, to make use of our main inspection organization for the products with which the A.I.D. is concerned. I think it is a measure of the respect that we feel for his Department that we have established a separate inspection organization.

I would first like to clear up any misconception that the main inspection department (I am not referring now to the approved A.I.D. inspection) is in any way concerned with, or has any responsibility for, production. It has not. It is responsible to the management, and by that is meant, in effect, the general management of the factory. It has contacts outside the factory direct with our selling organization and therefore with our large number of customers. The inspection is divorced from matters of economy and output, but it does observe standards not necessarily set by outside bodies, except through this customer contact. The standards are laid down by the management of the company, including the sales organization through the customer relationship.

If we did not have an independent inspection department for the rather specialized materials that go into the aircraft industry and into some of the other defence services, those inspectors would become less accurate in their knowledge of the requirements of those particular industries. It would be confusing for a set of inspectors and the chief inspector in

charge of them to have to switch their minds from one standard to another. There is only one standard for the A.I.D.; it is laid down largely by specification, largely by contacts direct with the aircraft builder, and a particular mental attitude is brought to the inspection of that type of product.

Dr. Singer has remarked, I think with regret, on the few examples of control systems in use, at least as disclosed by the present series of papers, and states that less examples are quoted than was the case in the previous two symposia. That is inevitably so because of the type of operation involved. I do not think that processes such as guillotine shearing, roller levelling, stretching, and so on, lend themselves to the measurement of error as the process proceeds and to the taking of steps to correct the error—unless I may be regarding control systems in too narrow a sense. I am, of course, excluding statistical control systems. We do, as adequately as we can (and this is in reply to the point raised by Mr. Smith), exercise statistical control of quality, and not only of quality but of our production conditions. Scrappages are statistically under control in our factory, for example.

Dr. Singer also raises the question whether the process of partial annealing, or temper-letting-down, lends itself to automatic control. Although the process itself—i.e. the temperature attained, and the time for which the charge is held at the required temperature—may be automatically controlled, and to some extent is controlled by present methods, one still would not have a precise process. Temper-letting-down is not so well defined in regard to the final mechanical properties of the material as the more conventional processes of temper-annealing and temper-rolling. Temper-letting-down is so much affected by the earlier thermal and cold-working history of the metal—which, when coils weighing 1–2 tons are involved, can vary even throughout a coil—that I do not think that by automatic control of an advanced type we should get precision of results.

Mr. Smith regrets that most of the papers have completely neglected any reference to control of composition. My impression is that this was not within the terms of reference of the present authors. We were not concerned with casting or melting, which is the point at which the composition is controlled; and, I think rightly, it has been assumed that the metal sent forward through the earlier stages of pre-heating and hot and cold rolling or extrusion is of the right composition when it reaches these terminal operations of heat-treatment, shearing, &c. I am rather concerned at Mr. Smith's remark that the paper by Mr. Field and myself gives the impression that the final operations with light-alloy sheet and extruded sections, and so on, are easy to control. They are not easy. We have got used to them, but constant vigilance is necessary. If departures from recognized procedures are not detected as soon as they occur, the rot is liable to set in and we as a Company may be involved in tremendous loss—or, worse still, our customers may be involved in loss.

That brings me to the general point raised by Mr. Kayser that our aim should be to produce a dead uniform product. I can assure him that there must be differences in products, as there are differences in alloys, in gauges, and in tempers for various uses. But for any particular specification our aim—we do not completely achieve it, of course—is uniformity.

Mr. Smith asks whether we have any experience of the R.A.E. assessment of flatness. We have no experience from the point of view of applying it, as I understand that assessment. I imagine it to be a three-point measurement of departure from flatness with the material laid on the surface of a table, or alternatively it is made by bending the sheet round a large-diameter former and measuring departure from flatness by putting a straight edge on it. We have operated both methods for investigation purposes, but not as a routine test for flatness. We judge flatness visually and, in bad cases, by feel. The sheet is laid flat and viewed at a very acute angle to the surface.

Mr. Smith also raises a point about our experience with controlled atmospheres and our comment that an oxygen-free atmosphere has its use or is desirable. I will admit that there is some difference of view within our Company as to the

precise purpose of a controlled atmosphere and what it achieves. We do not employ furnaces with controlled atmospheres, but we have seen them in operation elsewhere, and have not been able to find out from other users what particular purpose that controlled atmosphere serves.

We all know that magnesium-containing alloys stain when heated above certain minimum temperatures, presumably owing to oxidation, and controlled-atmosphere furnaces have been developed, in North America in particular, to prevent oxidation-staining of such material. I understand, however, that the reason they were specially developed for those alloys is that, with modern high-speed strip-rolling methods, a substantial film of oil is inevitably left on the strip. It is desirable to drive the oil off, and this requires a fairly long time at a fairly high temperature. Such a high temperature would be very detrimental to the magnesium-containing alloys, and it is for that reason that the controlled atmosphere was specially developed and is fairly widely used. However, some of my colleagues hold that the controlled atmosphere in itself will reduce oil-staining as distinct from oxidation-staining of magnesium alloys.

Mr. FIELD (*in reply*): I should like to assure Mr. Kayser that only prime-quality material which fully complies with the specification is supplied to the aircraft industry. We do discard beforehand material unfit for finishing, such as material received under gauge; unfortunately, our own material.

Mr. Kee has referred to edge bow and to the two grades of tolerance of $\frac{1}{4}$ in. and 1 in. maximum bow on 10 ft. It is easy to obtain 1 in., and $\frac{1}{4}$ in. is reasonable. It is very important that the length measurement should be 10 ft., because a difference of 1 ft. or even 6 in. can lead to a big error. It all depends on the strip rolling, and there is no great difficulty with modern mills in attaining $\frac{1}{4}$ in. Measurement can be made when necessary by running the strip between two 10-ft. steel straight edges, and occasionally stopping the strip to check its straightness.

Mr. Bushell has said that metals are unreliable, but if we look back into pre-history we shall find that they are the most reliable materials, better than wood, flint, stone, and leather, and they do not behave too badly now. Statistical variation is always with us. The effect of stretching on tensile properties is quite small. Measurements on heat-treated sheets, which should show the biggest effect of stretching, reveal a change of less than $\frac{1}{4}$ ton/in.² on proof stress and tensile strength. Mr. King has pointed out that a stretch of up to 2% assists subsequent surface machining by reducing distortion.

In reply to Mr. Bushell's point about stability of cold-worked tempers, a small diminution of properties after cold working is found in aluminium-magnesium alloys, which may be accelerated by thermally "stabilizing" at a low temperature, but, in general—for instance in half-hard rolled pure aluminium—the experience is that the temper is stable.

Mr. Bushell questions the annealing temperatures quoted in Table I (p. 207) and refers to narrow heat-treatment temperature ranges. More latitude is possible in annealing than in temper-letting-down or heat-treatment conditions, and it is found by initial check that with the furnace temperatures and times given, the resulting metal temperature is approximately as stated and gives a satisfactory anneal.

In regard to press-quenched and furnace heat-treated extruded sections, in each case final tests are carried out, and the requirements of the consumer are met, and certified when required.

There should be no difference in comparative distortion in heat-treatment between rolled and extruded bars, but complex thin extruded sections would distort in solution-treatment more than solid round, square, or rectangular bars, and would be less easy to rectify.

The point brought out by Dr. Bramley as to the restriction of ageing by the presence of water on the metal is of interest, but,

of course, this could apply only to natural or room-temperature ageing.

With reference to temper-letting-down, it is our practice to put in a contact pyrometer, and a flat, thin pyrometer which will do no damage is inserted into the sheets. As stated in the paper, it is a matter of trial and error to find what temperatures and times will give the right results for various materials. As to the effect of the letting-down in these conditions, the difference between the half-hard temper is 3 ton/in.² on the $1\frac{1}{4}\%$ manganese alloy and 1–2 tons/in.² for the magnesium alloy. The reason for using such a low temperature for the latter half-hard material is that the starting temper is close to what is finally required.

Mr. Bushell refers to surface qualities. There are many grades in the industry, ranging from sheet in which no blemish can be seen, through fully lustrous, oil-free sheet, to commercial sheet, which is not oil-free, and there are also grey and satin finishes. There are various degrees of flatness, from the finer-quality sheet to the commercial sheet and the type of sheet where flatness is not of much importance. We do receive special demands for flatness. The trained eye is most effective in assessing it. Some sheets are put on a surface plate as the basic flatness and a large scalped aluminium block is useful for this purpose.

Our method of grain-size assessment has been questioned. The table given is purely empirical, and the suggestion that there should be a generally recognized standard of values is a very good one. It is applicable primarily to the pure metal and to the $1\frac{1}{4}\%$ manganese alloy, but it could perhaps be adapted to the other alloys.

Mr. Murphy has referred to the secondary recrystallization phenomenon. 90% reduction will favour this secondary recrystallization. Much of the aluminium foil material is rolled to that reduction, and there is a risk of recrystallization occurring if the temperature is too high.

The information regarding the grey surfaces of aluminium tubes is of great interest, but this is a general phenomenon and does not depend on the handling. It is definitely a metallurgical phenomenon allied to the reticulated surfaces obtained on rolled strip as a result of its not entering the rolls squarely. If the material is inserted from above, the upper surface will be slightly reticulated or covered with minute cross scratches, which give it a grey appearance.

On the question of the effect of iron and silicon on grain-size, we agree that silicon is less important, but before the iron content was raised there was a grave risk that if the silicon content was too high and the iron too low, increased grain-size would result, and so the iron:silicon ratio came into the picture. Mr. Phillips* has been instrumental in showing the considerations involved. Much of the aluminium in commercial use today contains fairly high iron and fairly low silicon contents, and it gives a fine grain-size.

The lead bath to which Professor von Zeerleder has referred was purely experimental and is not used in commerce.

Mr. King's statement that changes in work-roll balance, due to variation in hydraulic pressure, affect the camber on the rolls prompts the supposition that if the hydraulic balance were gravity-accumulator-loaded, the pressure would remain constant.

In regard to Mr. Matthewson's remarks on independent control of inspection, it is agreed that final inspection should be under independent control, but it is considered best for intermediate or process inspection to be under the operating department. The more promptly the results of inspection are notified to the production staff, the better.

Mr. MILLER (*in reply*): I should first call attention to the fact that in Fig. 7 of my paper (p. 230 of Vol. 83 of the *Journal*) the bottom curve should be labelled 7500 and 15,000 lb./in.² not 7500 and 1500 tons/in.².

I would like to point out that the type of test considered under (e), p. 229, has recently become the subject of A.S.T.M.

* H. W. L. Phillips, *J. Inst. Metals*, 1942, 68, 86 *et seq.*

specification 279-53T. The test has been simplified somewhat from the procedure described in the paper, but the issue of this specification shows the importance now attached in America to stiffness tests on wire material.

Mr. Smith has pointed out some pertinent factors in connection with surface quality, and Dr. Bramley has drawn attention to differences in technique in the rolling and processing of copper and aluminium wire rod. In assessing surface quality we are dealing with something which is not tangible, and it is difficult to arrive at standards of comparison. Mr. Smith has suggested that it would be better for the copper industry to ensure perfect rolling conditions so as to eliminate the necessity of surface rectification. This is achieved in aluminium rod rolling according to Dr. Bramley.

It should be pointed out that differences in techniques in processing copper and copper alloys, as compared with aluminium and aluminium alloys, are also to be found in strip and sheet production. The need for surface dressing is entirely eliminated in the latest aluminium plants, whereas surface dressing is applied extensively in copper alloy fabrication.

In regard to rod rolling, it would appear that by restricting breaking-down passes to the order of 25% there is a complete avoidance of fins when rolling aluminium; the lower temperature and supply of lubricant solutions to the rolls are also helpful. In copper rolling the conditions are such that passes sometimes exceed 50% in the breakdown stages, and it is inevitable that there are slight fins, which are later considered objectionable under certain circumstances.

Thus, for high-quality copper wire production it is advisable to adopt a surface-rectification process on the hot-rolled rods; however, the quality of the latter is quite satisfactory for at least 90% of industrial requirements. For co-axial cable products, as mentioned by Mr. Smith, surface rectification on rolled rods is essential, or alternatively the initial hot-working process can be that of extrusion, which gives a satisfactory surface.

I have the opinion that spring-back is influenced neither by the method of drawing nor by the tools employed. It is a feature encountered only with annealed products and it depends on the conditions prevailing during annealing; deformation at a later stage is also of major importance. In certain processes, fine-gauge wire may be required to pass over a considerable number of pulleys, so that there is a considerable total length of wire under what might be a high load. If any stretching occurs, then it is inevitable that work-hardening is introduced, and this affects the spring-back most noticeably.

Mr. Bradbury has pointed out some differences in practice in the nickel and copper industries; it seems that economics alone account for the different views concerning strand-annealing. Vacuum-annealing plants have been marketed by at least two Continental manufacturers, who claim that they completely eliminate the stickiness of copper wire. Mr. Ström has provided useful information on experience with such furnaces, and, although he makes a reservation, he confirms that they have an advantage in this respect. To other disadvantages of vacuum-annealing as mentioned in the paper, Mr. Ström adds that of a longer cooling cycle.

I agree with Dr. Bramley in regard to the advisability of avoiding copper dust particles on aluminium wire, because of the adverse effects on the corrosion-resisting properties of the latter. In regard to the deposition of objectionable products from lubricants, these can definitely be attributed to the heavy mineral and vegetable oils customarily used in the drawing of aluminium wire. Further efforts should be made to develop less objectionable lubricants; for fine-gauge aluminium wire drawing there is the possibility of employing water-soluble lubricants, as in the case of copper wire drawing, although this practice is considered quite revolutionary.

The contributions of Mr. Norrö and Mr. Ström confirm the attention being given to the production of copper wire having constant spring-back characteristics. The routine examination of casts of copper so as to check the annealing characteristics is commendable, though I am doubtful whether the adoption of 1-hr. annealing treatments is satisfactory. For

fine-gauge enamelled-wire manufacture, the only annealing which occurs is in the course of stoving in the enamelling ovens. Therefore there is a better case for studying annealing times of 1 or 2 min. at a high temperature. It is my view that in the case mentioned there is a direct relationship between the composition of the copper, the annealing characteristics, and the springiness properties of the product. With other products there may not be a direct relationship.

Mr. HYSEL (*in reply*): With reference to the general comment by Dr. Singer and the detailed comment by Mr. Smith, which are in the nature of a criticism of over-simplification, we are very sorry if we have conveyed the impression that metal manufacture in any of its phases is a simple problem. Lack of space prevented us from giving more details of the particular process to which Mr. Smith has referred, namely, the annealing of copper and brass strip. Tables I, II, and III were intended to convey the types of annealing programme used to avoid

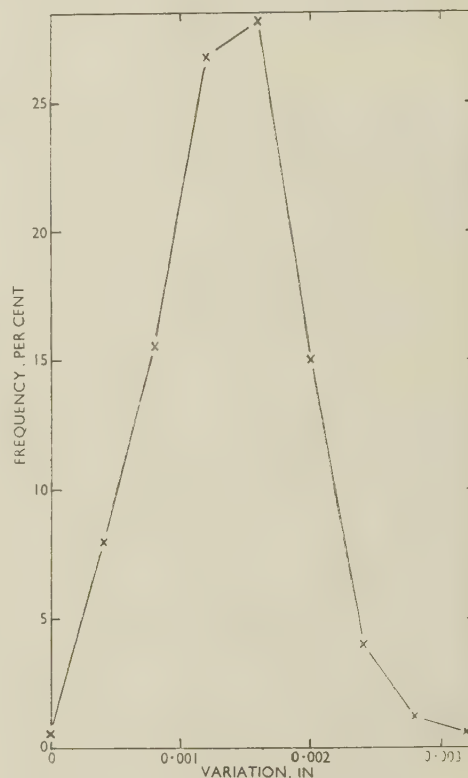


FIG. J.

the problem of sticking. It is quite true that a variation in batch sizes affects annealing programmes, and variation of alloy composition also gives rise to problems.

As regards the accuracy of slitting in the manufacture of co-axial cable, it has been suggested by both Mr. Smith and Mr. Kee that 0.0004 in. is an insignificant margin. In general such fine limits may be insignificant, when dealing with normal commercial tolerances on width, but in this particular case fine tolerances of -0 to $+0.003$ in. are imposed, and we had some difficulty in slitting within that tolerance and avoiding more than negligible rejections. I think it will be accepted that with a given set of cutters it is very difficult—I might almost say impossible—to slit a strip narrower than the set width of the cutters. For that reason it is our normal practice to set up cutters at the bottom end of the permitted range of tolerance.

A statistical examination of the width of several batches of hard strip produced a histogram of the kind shown in Fig. J. It will be seen that the slope of the curve is much steeper at the narrow end of the range. It was found that in the range of

0.003 in., the effect of the shrinkage on width of 0.0004 in., which occurs during annealing, becomes appreciable if the proportion of coils liable to rejection on the left-hand side of the curve is considered. It is for this reason we think it worthy of note that an increase in strip width of 0.0004 in. produces a greater percentage of acceptable material.

Mr. Kee has referred to the abnormal grain growth experienced in some forms of chromium copper. I think that his suggestion of uneven amounts of cold work across the section contributes largely to a possible explanation of the difficulties, mentioned in the paper, which are encountered in the manufacture of some forms of commutator segments where the ratio of thick to thin edge is particularly high. We do not experience much trouble with chromium copper in round and square-section rod. Such grain growth is a difficult problem to control during the solution-treatment stage.

Mr. Kee also comments on the danger of overageing chromium copper. We agree that for a plain chromium copper 450° C. is the optimum temperature. Our experience, in common with that of others, is that there are benefits to be derived from the inclusion of impurities. Mr. Kee mentions sulphur and silicon. We have found silicon to be advantageous, and this explains why overageing is not met with where precipitation-hardening is carried out at 475° C.

Mr. King refers to the control of pickling processes. Mr. Miller has already dealt with some aspects of this. I should like to go a stage further back than pickling, to the control established during the last decade on the final annealing in batch-type furnaces and electric furnaces, and on the use of more suitable lubricants, thus producing material less susceptible to the old trouble of the brass manufacturer, i.e. fire-staining. This has simplified the problem of producing satisfactory pickled strip. So far as pickling itself is concerned, a great deal has been done with continuous pickling, "strand" pickling, the control of pickle solutions, and the use of electrolytic recovery plants working in conjunction with pickle baths. All these tend to give a more uniform process and, as a consequence, a better-finished product.

Mr. King also mentions an interesting point, viz. the use of stretching to overcome subsequent distortion in machining. We have no experience of this means of overcoming a somewhat disturbing problem. The example cited in our paper referred to rather heavy blocks of phosphor bronze, about 12 in. wide \times 2 ft. long \times $\frac{3}{4}$ in. thick. These are not, I submit, really suitable for stretching, although I imagine that machinery could be devised to produce the necessary distortion. We have no practical experience of the application of such methods to rolled plate.

Mr. COLLIER (*in reply*): I should like to thank Mr. Bond-Williams for his contribution on measurement, particularly of commutator bars. This presents quite a number of problems, and I do not think we should rely too much on trying to measure what we call the thin edge. We prefer angle measurement and thick edge.

Mr. Kee has mentioned edgewise curvature or bow on strip. That gives considerable difficulty and we shall always want a tolerance on that curvature. He said that he did not know of any specification. I think that the British Standard specifies $\frac{1}{8}$ in. in 6 ft., and we can reasonably work to that, but with a finer tolerance it becomes a special job and may involve more expense. Recently I came across a draft specification of the South African Bureau of Standards asking for an edgewise curvature of zero. I think we must object to any such specification being introduced.

Mr. Berry has referred to the figures quoted for mechanical properties of extruded aluminium bronze to D.T.D. 197A in Table V, particularly the low elongation figure of 15%. The bar from which the tests were made was extruded on a press of only 600 tons' capacity and a relatively high extrusion temperature would be necessary, which no doubt would result in low proof and elongation figures in the extruded-only condition. Some typical test values obtained on rods extruded

on a press of 2500 tons' capacity, where the extrusion temperature would be considerably lower, are set out in Table B:

TABLE B.

Test Ref. No.	Dia., in.	0.1% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Elongation, % on 2 in. ($4\sqrt{A}$)	Average Brinell No. (2-mm. ball, 120-kg. load)
1	2	30.2	48.1	16	249
2	2	25.6	47.6	20	218
3	1 $\frac{3}{4}$	24.4	45.3	27	199
4	1 $\frac{3}{4}$	25.7	46.7	20	202

It is interesting to learn that Dr. Messner has encountered possible instances of season-cracking in copper tubes. If produced by the normal methods, the tubes are free from stresses likely to cause failure in service, and there should be no necessity for a stress-relieving treatment.

He also refers to incomplete recrystallization of 63:37 brass tubes. I do not think the annealing time of something less than 30 min. at 520°–580° C. is long enough to ensure complete recrystallization, and this would apply, whatever type of furnace were used for annealing.

I would agree with Dr. Messner that springiness tests usually applied to spring material often lead to uncertain results. British Standards do not demand any special tests for springiness, and it is general to specify only minimum tensile stress with hardness and bend tests.

Dr. BETTERIDGE (*in reply*): Mr. Thompson has raised the question of whether the eddy-current method is applicable to bars other than those with a circular cross-section. We have not up to the present used it for other than round-section bars, but it seems clear that it would be applicable, even though the sensitivity would vary for defects at different points round the periphery of a bar owing to the variation in density of the eddy currents with the change in section; that is only an opinion and we have no direct information.

Mr. COUND (*in reply*): I should like to deal briefly with control of quality in the pickling of nickel alloys. The pickle solutions used vary with the type of alloy; some have been discussed in the paper.

It seems that the essence of pickling is completely and rapidly to remove the oxide skin without solution of the underlying metal, and control in pickling must have these objects in view. For a given pickle, the two main variables are time and temperature. When an increase in time indicates that the pickle is becoming exhausted in respect of one of its essential constituents, for a limited number of immersions this deficiency may in some pickles be made good by additions of that constituent. Eventually, however, the whole pickle must be renewed.

Dr. Sachs has referred to the test for gas-free nickel. This was developed some years ago before vacuum-extraction of gases was developed; it is semi-quantitative, and has served a very useful purpose in distinguishing between gassy and non-gassy nickel, as indicated in the text of our paper and in Fig. 7 (Plate XXXVII). The firm to whom this wire was supplied has recently put the test on a more nearly quantitative basis. Dr. Jenkins has discussed the test in a recent paper.*

Mr. EDMUNDS (*in reply*): Mr. Martin has declared that forging is still an art, to which has been allied the precision of engineering tools and the precision of metallurgical knowledge of materials. There is a difference between the practice in the United States and the practice in Great Britain. Here we do not have the demand for the enormous number of forgings typical of United States production, and therefore the production of forgings is strictly individual. From that point of view, there cannot be in the forging field of operations the same demand

* I. Jenkins, *Metal Ind.*, 1955, 86, (1), 3; (2), 23.

for intensive instruments for the detection of flaws. Quality in forging depends upon the past history of the material, as defects which can arise in the forging operation are relatively few. So today quality lies chiefly in the material which is placed in the forger's hands.

Mr. Smith and Mr. Bradbury have referred to die life. This is a matter of design and mass; temperatures are secondary. If sharp lugs and bosses exist, they are bound to cause cracking in the die.

I entirely agree with Mr. Chadwick's classification of blisters. In answer to his question, I think it would be better to lubricate the die, where the lubrication could be more easily applied.

Mr. Martin asks about the present tendency to utilize polishing followed by chromic acid anodizing. There again, while I am in entire agreement with everything being done to ensure a perfectly good forging going out, many of the defects which occur in forgings originate in the stock, so would it not be better, instead of individually polishing complicated small and large forgings to apply some sort of polishing operation to the individual sections in the bar form? That would be very much easier if it were done on a uniform round or square bar, and from the economic point of view it is worth considering whether it should not be carried out earlier.

I am glad that Mr. Martin has confirmed our view that rolled bar is quite good stock. We have found it to be so. But our impression is that nowhere in this country is it possible to obtain it.

Dr. Sachs wants to know why dies are hand-polished. Dies are hand-polished after the preliminary work has been done for the simple reason that it eases the flow of metal in the die, prevents sticking in the die, and leads to increased die life. The amount of time spent on the operation depends on whether the worker can get his hand or only a finger into the die.

Mr. LLOYD (*in reply*): We agree with Mr. Chadwick that the only way of differentiating with any certainty between the

different types of blister is by micro-examination, and we have emphasized the value of such examination in preventing the further occurrence of the type of defect referred to. He commented on our Fig. 11, showing overheating in extruded bar. This is a longitudinal micro-section, but perhaps the field was not ideally chosen to illustrate the directionality of the structure. This, combined with the fact that the eutectic is completely undistorted by working, may have suggested to him that it was a cast structure. We can assure him that a longitudinal macro-section from the bar showed quite a directional structure.

Mr. Thorley asks for our comments on a particular type of defect which he calls "flash-line defect". His Fig. F (Plate LXXXVI) shows a semicircular light patch, and he suggests that this type of defect may be due to oxide film. We do on occasion find oxide films which we presume have originated at the casting stage, and we have stated that these may or may not come to the surface at the flash. In one particular case of a roughly cylindrical forging several inches in diameter, there was no trace of any defect at the flash line, but it was subsequently returned to us by the customers, who discovered a crack on boring into the forging from one end. We took a series of transverse macro-sections through the forging and found that throughout the length of the forging there was a roughly circular oxide film, which we presume originated in casting. It did approach the flash line but had not reached the exit part of the flash.

With regard to the particular case which Mr. Thorley mentions, we should have thought that an oxide film would show up on fracture as a dull patch, not a light patch. Two other explanations suggest themselves: local overheating in the flash line, which we have mentioned, and stress-corrosion failure. I do not know under what conditions this forging had been previously maintained, but we have found that stress-corrosion failures exhibit a similar type of fracture, a light patch of the same shape as that illustrated.

Discussion

Fatigue *

Mr. T. BROOM,† M.A. (Member), and Mr. J. H. MOLINEUX,‡ M.Sc.: The disappointingly poor fatigue properties of precipitation-hardened alloys have often been ascribed to some form of over-ageing occurring during fatigue testing,§ and Dr. Hanstock is to be congratulated on a convincing demonstration that over-precipitation can be caused by fatigue. An atomic mechanism for this process has been put forward,|| which depends on theoretical and experimental evidence¶ for the generation of vacant lattice sites by moving dislocations. It is suggested that the first stage in the fatigue of alloys of high yield stress is the activation of a dislocation source. The probability of this happening after a number of cycles of stress may crudely be taken as inversely proportional to the difference between the yield stress and the applied stress. When one or more dislocations move, they generate vacant lattice sites which at room temperatures are mobile and can promote the local establishment of equilibrium by causing over-precipitation. In consequence, further dislocation movements can occur, and the process can be described as "autocatalytic", leading to the rapid formation of a "soft spot". The production of a fatigue crack is not

understood, but there is much evidence to show that the necessary condition for crack formation is the movement of dislocations.

This picture is consistent with the damping-capacity changes shown in Fig. 2 (p. 12) of Dr. Hanstock's paper, where precipitation and crack propagation occur catastrophically right at the end of a test. The problem of fatigue in high-strength alloys then seems to be the elucidation of the factors which permit dislocations to move and initiate damage when the externally applied stress is much lower than the macroscopic yield stress. It has been suggested** that the gross intermetallics in D.T.D. 683 alloy act as internal notches, giving rise to local stress concentrations. Dr. Hanstock's micrographs show no clear evidence of this, but his views on the point would be appreciated.

Finally, we would like to refer to some experiments carried out on specimens of D.T.D. 683 alloy aged at 135° C. for 5 hr. nearly to peak hardness and on specimens grossly over-aged by heating at 135° C. for 1040 hr.

Fatigue tests were carried out at 18° and -183° C. in an Amsler direct-stress machine with zero mean load. The

* Joint discussion on the following papers published in the *Journal*: P. J. E. Forsyth (1953-54, 82, 449); P. J. E. Forsyth and C. A. Stubbington (this vol., p. 173); R. F. Hanstock (this vol., p. 11); J. McKeown, D. N. Mends, E. S. Bale, and A. D. Michael (this vol., p. 69); J. W. Martin and G. C. Smith (this vol., p. 153).

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‡ Formerly Department of Industrial Metallurgy, University of Birmingham.

§ E. Orowan, *Proc. Roy. Soc.*, 1939, [A], 171, 79.

|| J. H. Molineux, *J. B'ham. Met. Soc.*, 1954, 34, 28.

¶ F. Seitz, *Advances in Physics*, 1952, 1, 43.

T. Broom, *ibid.*, 1954, 3, 26.

** J. A. Bennett and J. G. Weinberg, *J. Research Nat. Bur. Stand.*, 1954, 52, 235.

fatigue result quoted in Table A is the stress for a life of 10^5 cycles, S_5 , estimated in each case from not less than six results.

TABLE A.—Results of Tensile and Fatigue Tests on D.T.D. 683 Alloy.

Condition	Test Temp., °C.	Yield Stress, tons/in. ²	U.T.S., tons/in. ²	S_5 , tons/in. ²	S_5 /U.T.S.
Fully hardened {	18	31.2	37.5	18.0	0.48
	—183	43.5	45.4	30.4	0.67
Over-aged {	18	20.4	27.8	16.9	0.61
	—183	29.5	36.3	25.8	0.70

At room temperature the fully hardened and over-aged specimens gave nearly the same fatigue result, despite the difference in tensile properties, but at liquid-air temperature the difference in fatigue properties corresponds closely with the difference in tensile properties. At liquid-air temperature vacant lattice sites are virtually immobile and so cannot cause over-ageing in the fully hardened material. This work provides direct evidence for the supposition that over-ageing during fatigue has a controlling influence on the fatigue strength of precipitation-hardening aluminium alloys.

Dr. H. K. HARDY,* M.Sc., A.R.S.M., A.I.M. (Member): Several different types of artificially aged strong aluminium alloys give essentially similar fatigue properties. Dr. Hanstock, in the paper under discussion, has suggested that their metallurgical structure is unstable under cyclic stress. In his view, the nature of the changes produced by cyclic stressing is similar to that induced by a higher ageing temperature, except that the "over-ageing" caused by cyclic stressing occurs only in localized regions. Dr. Hanstock has produced photomicrographs (Plate IV) showing heavy precipitation adjacent to the fatigue cracks in D.T.D. 683 alloy. He suggested that the fatigue cracks were initiated in the soft low-strength regions produced by the cyclic stressing. Mr. Forsyth and Mr. Forsyth and Mr. Stubbington observed recrystallization of cold-rolled aluminium under the influence of cyclic stressing. The fatigue cracks occurred within the recrystallized regions.

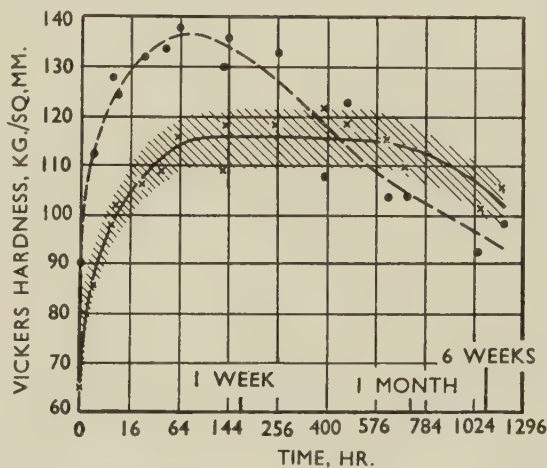
In deciding whether the cracks cause the soft regions or whether the soft regions provide sites for the cracks, it is necessary to remember that there may be sets of soft regions possessing different orientations with respect to the axis of the specimen. The localized nature of the soft regions prompts comparison with the creep behaviour of very high-purity aluminium-4% copper alloys in which the deformation was restricted to the grain-boundary regions depleted in solute by precipitation.† Shear along grain boundaries at 45° to the axis of the specimen led to intercrystalline fissures in grain boundaries normal to the axis. Suitably oriented sets of soft regions could cause stress-concentration effects and possibly superimposed tensile stresses, if their formation were accompanied by a volume expansion. On this basis, cracks would be initiated at the boundary between the soft and the unaffected regions, but would probably spread rapidly into the soft regions.

It is strictly relevant to point out that work-softening of a suitably aged alloy can also be caused by straightforward cold working. Fig. A—due to Wassermann‡—shows that the hardness of an aluminium-4.13% copper alloy aged at 150° C. for less than three weeks was increased by 10% cold reduction. After longer ageing times, however, the hardness

fell when the alloy was cold worked. Wassermann reported similar experiences with an aluminium-copper-magnesium alloy.

It can be postulated that cold work destroys the coherency between the matrix and the precipitate. Transfer to a more stable non-coherent precipitate would thereby be facilitated, and the reduction in the coherency strains would partly be responsible for the work-softening.§

It is quite reasonable to extend the argument to cover the effect of cyclic stressing on alloys hardened by an intermediate precipitate. Any "over-ageing" is likely to involve the formation of a more stable precipitate and the consequent further rejection of solute atoms from the matrix—a process markedly analogous to the "light phenomenon".|| There are three ways in which cyclic stressing could have this type of effect: (i) a non-coherent precipitate may be nucleated from the matrix; (ii) a coherent precipitate may be transformed into a non-coherent form by a monotropic transformation; (iii) the non-coherent precipitate may be rendered



[Courtesy Z. Metallkunde.]

FIG. A.—Hardness Values for an Aluminium-4.13% Copper Alloy Aged at 150° C. (After G. Wassermann.‡)

KEY.

- × Solution-treated and aged.
- Solution-treated, aged, cold-rolled to 10% reduction.

unstable and be forced to redissolve. Anomalously rapid diffusion occurs in many aluminium alloys at room temperature, and diffusion will probably be facilitated by the dislocation movements introduced by the cyclic stressing.

Mr. F. P. BULLEN,¶ M.Sc. (Junior Member), and Mr. R. B. DAVIES,** M.Sc. (Member): As members of a group studying fatigue, we are particularly interested in Mr. Forsyth's paper on the fatigue process in pure aluminium, as well as in his earlier work. Although many of Mr. Forsyth's observations are similar to our own, we should like to comment on certain aspects of his experimental techniques and interpretations.

In regard to testing conditions, we feel that certain features of Mr. Forsyth's vibrators and test specimens could have contributed to the structural distortions reported in the present and earlier papers. (Mr. Forsyth's earlier work,†† in particular, yielded metallographic evidence of extensive disorientations.) Some of our experiments have shown that anomalous effects are likely to result from fatigue tests on

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† A. H. Sully and H. K. Hardy, *J. Inst. Metals*, 1953–54, 82, 264.

‡ G. Wassermann, *Z. Metallkunde*, 1950, 41, 50.

§ B. L. Averbach, *Cold Working of Metals* (Amer. Soc. Metals), 1949, 282.

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H. K. Hardy and T. J. Heal, *Inst. Metals: Symposium on the Mechanism of Phase Transformations in Metals*, 1955, 1.

|| I. J. Polmear and H. K. Hardy, *J. Inst. Metals*, 1952–53, 81, 427.

¶ Scientific Officer; ** Experimental Officer, Aeronautical Research Laboratories, Melbourne, Australia.

†† P. J. E. Forsyth, *J. Inst. Metals*, 1951–52, 80, 181.

soft metals, when the tensile and compressive stresses are even slightly unbalanced.

We should like to ask whether Mr. Forsyth detected any permanent macroscopic distortions or dimensional changes in his test specimens after cycling. It would also be of interest to learn whether the un-notched specimens tested in his machines showed structural changes similar to those reported for notched specimens. With such information, it should be possible to determine whether the observed changes constitute essential characteristics of the fatigue process, or whether they are features typical only of a particular set of testing conditions.

We feel that multiple-beam interferometry is not entirely satisfactory as a technique for the measurement of slip displacements produced under fatigue conditions. In the first place, the light microscope proved incapable of resolving the finer bands contained within the coarser bands constituting "striations", while the ultimate lamellar structure was not resolved even by electron microscopy. Multiple-beam interferometric techniques were therefore adequate only for the measurement of slip displacements across the coarse bands. Secondly, the major difference between the slip movements occurring in these experiments and those described by Brown* and others lay in the occurrence of slip in opposite directions on neighbouring lamellae within a band. Thus, the slip displacements measured by Mr. Forsyth would represent the algebraic sum of a number of lamellar slip displacements. The quoted slip-band displacements (of the order of 2000 Å.) could be reconciled with those discussed by Brown either by the occurrence of an excess of slip movements in one direction, or by the summation of small differences in the distance slipped along individual lamellae.

In regard to Mr. Forsyth's suggestion that every possible plane within a striation has been brought into action, some of our experiments may be of interest. We have found that after further cyclic straining of copper specimens which had been repolished during interruptions to tests, the original pattern of striations reappeared.† Since the striations increase in width at a relatively slow rate during cycling, we should have expected to find narrow bands unless further slip had occurred within the original striations. The possibility of further movement along previously slipped planes within the striation seems less likely than the alternative that slip occurred on previously inactive planes within the original striation.

We have carried out a few experiments on cyclic straining of aluminium, but have not detected boundary migration or polygonization, although large-scale boundary migration was observed during tests on zinc.‡ We have not found kink or deformation bands on copper specimens fatigued at the higher frequencies.§ Such bands have frequently been linked with the occurrence of X-ray asterisms, and hence would not have been expected under these conditions on the basis of the results of Wood and Head.|| The greater facility with which kink bands form in aluminium may provide an explanation for some of the observed differences.

In his discussion of the X-ray observations of Wood and Head,|| Mr. Forsyth states (p. 452) that "The higher the frequency of cyclic stressing, the less was the initial deformation, and the more complete the recovery on completion of the cycle". We feel that a clear distinction should be made between: (i) the changes occurring up to the stage when the first cycle of maximum stress is completed (as studied by Wood and Davies¶), and (ii) the changes occurring during

repetitions of this stress cycle (as studied by Wood and Head||). Structural and dimensional changes during the loading period may be greatly restricted by building up the load in the course of a sufficient number of cycles, even under the low rates of stressing associated with ordinary "static" testing.¶ It seems doubtful, therefore, whether the "initial" deformation mentioned by Mr. Forsyth is significantly dependent upon testing frequency, at least within the ranges investigated by Wood and Head. Since the changes occurring up to the completion of the first cycle of maximum stress can be restricted so effectively, it follows that the "recovery" from such changes as do occur will be a relatively minor effect. There appears to be no direct evidence to support the contention that "recovery" of this type is greater at the higher frequencies. The researches of Wood and Head were concerned with the *net* structural changes occurring during alternating stress tests involving loading sequences designed to prevent net unidirectional strains developing during the loading stages at both high and low frequencies.

Mr. Forsyth draws the further conclusion that slip in one direction can be partially restored by a stress reversal, but this appears to be without foundation in the published work of Wood and Head|| (who confined themselves to X-ray-diffraction studies).

Mr. Forsyth has observed staining in the vicinity of striations (p. 453), and he attributes this to localized heating. We have observed similar staining phenomena during fatigue tests on copper at 21 c./min.

It seems likely that atmospheric attack may occur in areas where development of a slip "step" exposes a narrow strip of metal, unprotected by an oxide film, and that time of exposure may be no less important than local temperature peaks. The work of Gough and Sopwith** showed that atmospheric conditions, particularly the presence of moisture, influence the endurance of some metals to a marked degree. Possibly preferential corrosive attack in the vicinity of the slip bands may assist the development of a fatigue crack, and at the same time roughen the edges of the slip surfaces, thus rendering difficult the interpretation of high-power electron micrographs. The possibility would seem to justify a careful electron-microscopic examination of specimens tested *in vacuo*.

Mr. B. STRÖM †† (Member): The suggestion put forward by Mr. Forsyth and Mr. Stubbingon that a substructure is formed during the fatiguing of super-pure aluminium in regions where cracks will later occur, is interesting. So far, however, there are no indications that substructure formation is an inevitable stage in the development of fatigue cracks. Metallographic studies made by Craig ‡‡ with the electron microscope on fatigued samples of α -brass showed that cracks form in the slip bands, but no signs of a substructure were reported.

An investigation carried out in the laboratories of Svenska Metallverken at Västerås, on fatigued O.F.H.C. copper, showed that the cracks follow either grain boundaries or slip bands, as illustrated in Figs. B-E (Plate LXXVII). Subsequent etching or X-ray study of the samples, using the Guinier-Tennevin §§ focusing technique, did not reveal any polygonization or substructure formation.

Has the existence of a substructure in fatigued aluminium been proved by means other than the metallographic method? There is always a danger that the substructure as shown in Figs. 5 and 6 (Plate XXVIII) of the paper might be a polish-ing or etching effect.

* A. F. Brown, *J. Inst. Metals*, 1951-52, **80**, 115.

† F. P. Bullen, M.Sc. Thesis, University of Melbourne, 1952.

‡ F. P. Bullen, *Commonwealth Australia, Dept. Supply, Aeronaut. Research Lab. Rep.*, 1953, (**SM-218**).

§ F. P. Bullen, A. K. Head, and W. A. Wood, *Proc. Roy. Soc.*, 1953, [A], **216**, 332.

|| W. A. Wood and A. K. Head, *J. Inst. Metals*, 1951, **79**, 89.

¶ W. A. Wood and R. B. Davies, *Proc. Roy. Soc.*, 1953,

[A], **220**, 255.

R. B. Davies, *Commonwealth Australia, Dept. Supply, Aeronaut. Research Lab. Rep.*, 1953, (**SM-203**).

** H. J. Gough and D. G. Sopwith, *J. Inst. Metals*, 1935, **56**, 55.

†† Assistant Chief Metallurgist, AB Svenska Metallverken, Finspong, Sweden.

‡‡ W. J. Craig, *Proc. Amer. Soc. Test. Mat.*, 1952, **52**, 877.

§§ A. Guinier and J. Tennevin, *Acta Cryst.*, 1949, **2**, 133.

Professor R. W. K. HONEYCOMBE,* M.Sc., Ph.D. (Member): The most striking metallographic feature of fatigue is undoubtedly the formation of striæ, i.e. groups of slip avalanches constituting a band much broader than is normally observed in unidirectional deformation at room temperature. It appears that this phenomenon is characteristic of fatigue over a wide range of experimental conditions, whereas the formation of kinks and extensive polygonization is not necessarily so. However, the formation of concentrated regions of slip lamellæ is not confined to fatigue, and I suggest that it is a general characteristic of plastic deformation, at least in face-centred cubic metals, over a wide temperature range. It is true that the striæ produced in tension are not normally as pronounced as in fatigue, but if the temperature of deformation is raised to near the melting point the metallographic similarity is striking. Fig. F (Plate LXXVII) shows a high-purity aluminium crystal which has been deformed to only 6% elongation in tension at 500° C.; the concentration of slip into striæ is already quite pronounced. Again, under creep conditions, similar observations can be made on aluminium single crystals, but at temperatures considerably lower, e.g. 300° C.

The fact that in normal deformation striæ are pronounced at elevated temperatures suggests that temperature may play some part in the development of striæ in fatigue. There is much evidence that heat is generated in a fatigue specimen, particularly when the frequency of the cycle is high. A macroscopic rise in temperature of a few degrees could well correspond to a considerably higher temperature in the slip bands, and there seems no reason why high temperatures should not persist locally, even when the frequency of the cycle is quite low. The sliding of metal surfaces over each other presents a crude analogy, for here, even at low sliding speeds, hot spots are developed while the bulk temperature is practically unaltered.

Some other evidence for the development of local high temperatures on the slip bands during fatigue, can be found in the papers under discussion:

- (1) Grain-boundary migration near the ends of striæ.
- (2) Pronounced polygonization in striæ compared with other regions.
- (3) Localized precipitation in heat-treated aluminium alloys.
- (4) Extrusion of thin metal ribbon during fatigue.

I should like to mention two further points dealt with in Mr. Forsyth's paper. While the slip displacements in striæ may not be comparable with the measurements by Brown, the more recent electron-microscope work of Kuhlmann-Wilsdorf and Wilsdorf† has shown that the slip displacements in normal deformation can vary over a very wide range, so it is difficult to contrast the measurements from fatigue specimens. Finally, bearing in mind the so-called "slipless" flow which was supposed to be characteristic of creep until fine slip was detected, it is difficult to accept the statement that no fine slip exists between the striæ in fatigue. If fine slip does not occur, then it is hard to appreciate why slip should occur in widely spaced striæ.

Dr. A. P. MIODOWNIK,‡ A.I.M. (Student Member): Mr. Forsyth and Mr. Stubbington are to be congratulated on providing such painstaking observations of the fundamental microstructural effects of fatigue. There seems, however, to be some doubt about the interpretation of the microstructures. Much has already been said about the creation of soft spots by a local rise in temperature, and it seems to be generally assumed that a soft spot is particularly susceptible to cracking. This conclusion is not at all obvious.

By definition, a "soft spot" is capable of absorbing strain-energy; the mere existence of such an area can therefore hardly be a cause for cracking. If it is assumed that cracking

is the result of concentration of deformation in such an area, it would be begging the question to attribute it to the "soft spot". It also seems most difficult to explain the intensely localized nature of such deformation, as depicted in Fig. 22 (p. 175 of the paper).

In all probability the cause of cracking ultimately depends on the nature of the stress system on each distinguishable microstructural area; that is to say, on the degree of bi- and tri-axiality of stress, and on the shear stress and fracture susceptibilities of each structure present. It may well be that soft spots are brittle, but only in conjunction with the restraints built up by the harder surrounding phase areas.

An analysis on these lines is necessarily complicated by the continuous change occurring in these variables during the fatigue process. Assuming the existence of restraints adjacent to the coarsely polygonized areas, it would appear likely that fracture would start at the interface between the "soft spot" and the matrix. However, the observed central position of the cracks (Figs. 5 and 6, Plate XXVII) might suggest that the embryo crack was formed during the deformation which occurred before the onset of coarse polygonization; simultaneous growth of this crack and development of coarse polygonization would lead to the observed microstructure. It might not be out of the question that the embryo cracks act as sinks for internal stresses and so actually aid the coarse-polygonization process.

Dr. E. F. EMLEY,|| B.Sc., F.R.I.C., F.I.M. (Member): I am much interested in the general difference in shape of the *S/N* curves for ferrous and non-ferrous alloys. Some work carried out by one of my colleagues, Mr. D. J. Brown, on a wrought magnesium-zinc-zirconium alloy, not susceptible to age-hardening, showed that in the absence of either moisture or oxygen a ferrous type of *S/N* curve with true fatigue limit was obtained. This suggests that in air the phenomenon occurring during the fatigue testing of this magnesium alloy, at least, is corrosion-fatigue. It seems significant that whereas aluminium alloys in general show *S/N* curves continuously falling with time, as do magnesium alloys, the corrosion-resistant alloys containing 5 and 7% magnesium exhibit ferrous-type curves. The same applies to super-purity aluminium.

Whilst it is not suggested that corrosion-fatigue is the only factor responsible for continuously falling *S/N* curves, it may well play a more important part in the case of aluminium alloys than has been generally recognized.

Mr. FORSYTH and Mr. STUBBINGTON (*in reply*): Mr. Bullen has drawn attention to the fact that extensive disorientation may result from unbalanced tensile or compressive stresses. Our experience of fatigue testing pure aluminium in Haigh direct-stressing machines is that unbalanced loads of only a few pounds can produce remarkable elongation of the specimens. The methods of testing micro-fatigue specimens used in this work make it difficult to avoid unbalanced loads on the specimens, although these loads must be very small, as in most cases no permanent set of the specimen could be detected. The fact remains, however, that after a period of cyclic stressing polygonization and even recrystallization occur, whereas the small unbalanced loads themselves would not have produced these effects. We have shown that cyclic stressing can produce effects that would otherwise occur only at elevated temperatures. It will be seen from Forsyth's earlier work that only where the cyclic stresses are high does the formation of subgrains and creep play any part in the fatigue process. At lower stresses no association of subgrain boundaries with the crack path could be proved. It should be noted that even in the absence of an unbalanced load, unidirectional strain of parts of grains must be inevitable at a free surface. This is

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† D. Kuhlmann-Wilsdorf and H. Wilsdorf, *Acta Met.*, 1953, 4, 394.

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|| Chief Metallurgist, Magnesium Elektron, Ltd., Clifton Junction, nr. Manchester.

particularly so in grain aggregates subjected to high cyclic stresses. As regards Mr. Bullen's reference to the utility of multiple-beam interferometry, the limitations of this technique were in fact explained. Probably the most useful information obtained was not the slip displacements of the coarser bands but the existence of more homogeneous deformation between bands of this type. The fact that the horizontal resolution of the multiple-beam technique was not great enough to detect individual micro-slip bands was not important, as the electron microscope subsequently revealed their presence. The suggestion in the paper that all possible planes within a striation might be brought into action by cyclic stressing did not imply that they were activated in an orderly fashion starting from the first lamella and building outwards to form a striation. Mr. Bullen's experiments on copper show that this is not so. The photomicrograph* also shows this. This structure was obtained by fatiguing, repolishing, and then re-fatiguing. I agree with Mr. Bullen that the continuous development of slip steps exposed to the atmosphere unprotected by an oxide film may cause a "build-up" of the oxide along these bands. An attempt was made to simulate the yellow stains along slip bands on fatigued aluminium by heating freshly polished aluminium specimens. It was found that it was necessary to approach the melting point before similar staining occurred. It is also important to note that what may be described as staining from a cursory low-power microscopic examination may often be resolved into the now familiar network pattern when examined with a higher numerical aperture. It would seem that this regular deformation pattern can act as a diffraction grating, thus giving spurious effects.

Mr. Ström refers to the fatigue of α -brass in which the fatigue cracks started in the slip bands. No polygonization would be expected in this alloy nor is it necessarily found in many aluminium alloys, where failure is often influenced by the instability of the material to cyclic stresses. The existence of a substructure in fatigued aluminium was confirmed by ordinary back-reflection and also by microbeam X-ray techniques. This was reported in an earlier paper.†

We are interested in Professor Honeycombe's observations on slip striations produced in aluminium by tension at elevated temperatures and agree that a temperature rise along fatigue slip bands might account for this similarity in behaviour.

Dr. Miodownik has suggested that soft spots can act in a brittle manner only when surrounded by a harder matrix. We would agree with this, and point out that it is precisely under these conditions that fatigue fracture occurs. More recent work on aluminium alloys shows a similarity in behaviour when a solute-atom-depleted region is surrounded by a stronger matrix. His reference to the cracks shown in Figs. 5 and 6

(Plate XXVII) is interesting. We should add that this recrystallization and heavy deformation is accompanied by an eruption of this region which makes any hypothesis on the order of occurrence of events very difficult. It is also possible that, after removing some of the surface by electropolishing, one is then viewing the crack in a position it has attained after it has propagated a small distance. During this propagation it may have caused a more symmetrical growth of the grains around it. In the more simple case of cracks appearing in striations, it has been noticed that they almost invariably occur at the striation edge.

Dr. HANSTOCK (*in reply*): The static strength of some precipitation-hardening aluminium alloys is abnormally and gratifyingly high, and this high strength is usually accompanied by a modest increment in fatigue strength. I make this statement to put into a different perspective the remarks of Mr. Broom and Mr. Molineux. Of course an improvement in fatigue strength proportional to the improvement in ultimate strength would be welcome. I have attempted to demonstrate that this proportional increase is not obtained for a particular reason, but this demonstration should not be taken to indicate any deficiency in the actual magnitude of the fatigue strength of this type of alloy. I am grateful to Mr. Broom and Mr. Molineux for the supporting evidence contained in Table A of the combined effects of temperature and cyclic stressing on precipitation stability.

I have no evidence that intermetallics in D.T.D. 683 act as internal notches, and the small fatigue cracks that I have observed do not appear to be associated exclusively with the intermetallics, whereas they are always associated with bands of precipitation.

Mr. Molineux's picture of the mechanism of precipitation under the action of stress may well be true; diffusion preceding precipitation may reasonably be supposed to be facilitated by the creation of vacant lattice sites. As a further development of the role of dislocations, I would like to have an explanation of the characteristic variation of damping with stress in terms of dislocation theory.

Dr. Hardy's reference to the location of the fatigue crack with respect to the region of precipitation, raises a point upon which I certainly would not wish to be dogmatic. Although in the paper I say somewhat loosely that fatigue cracks form within the bands of precipitation, there is some evidence, not included in the paper, that the appearance of a fatigue crack at the boundary of the precipitated region is a frequent but not an exclusive occurrence. However, as precipitation may develop further after the formation of a crack, possibly as a consequence of generation of heat, the initiation of a crack may be always, as Dr. Hardy says, at the boundary.

Discussion

Twinning ‡

Mr. P. E. MADSEN, § B.Sc. (Junior Member): Dr. Churchman has suggested in his paper that the mechanism of thermal detwinning is analogous to grain growth, and that whether a twin grows or becomes absorbed depends on the relative amounts of strain in the twin and the matrix grain. Might not a more simple explanation be that the growth or absorption of a twin depends on the reduction of the free energy of interfaces, exactly as in grain growth, and that strain energy has a negligible effect?

Some observations on the microstructure of worked α -uranium after annealing lend support to this hypothesis. When lightly deformed specimens are heated, it is observed that the intersection of twin and grain boundaries tend to

migrate down the twin boundaries (Fig. A, Plate LXXXVIII). If the twins are thin and widely spaced, the boundary between the twin and adjacent grain tends to contract to a point. Further boundary adjustments will cause the twin to become free from the grain boundary and eventually lead to its absorption by the grain. Where twinning is more profuse, similar adjustments at the intersections of twins and grain boundaries may cause adjacent twins to become joined, the boundary to migrate into the more heavily twinned grain, or even the growth into the grain of a twin from a neighbouring grain.

Working also produces junctions of interfaces at twin intersections which are not in equilibrium under surface-

* *J. Inst. Metals*, 1953-54, 82, Plate LXX, Fig. 22.

† *Ibid.*, 1951-52, 80, 181.

‡ Joint discussion on the papers by A. T. Churchman

(*Journal*, this vol., p. 39); E. Billig (this vol., p. 53); and R. L. Woolley (this vol., p. 57).

§ Atomic Energy Research Establishment, Harwell, Berks.

energy requirements. An interesting example of this is the intersection of (172) and (172), and (172) and (172) twins, which Cahn* has shown can cross without change of direction. At most angles of sectioning, the central secondary twin appears as a quadrilateral with each corner consisting of a 4-ray junction of interfaces. On annealing, such junctions would be expected to decompose into two 3-ray junctions with a fresh interface joining them (as in the analogous stage of grain growth), and the secondary twin would become a hexagon. Fig. B (Plate LXXVIII) probably shows type-{172} twin intersections after some growth.

Kink-band boundaries also possess a significant surface energy, since intersections of kink and grain boundaries show similar displacements to intersections of twin and grain boundaries on annealing. This may explain cases which have been reported of twins swelling on annealing, if the matrix has, as Dr. Churchman suggests, undergone more deformation than the twins.

Dr. S. E. MAYER,† B.Sc., A.I.M. (Member): In connection with Dr. Billig's paper I would like to comment on the relative importance of twinning due to impurities and that due to stress.

While it is quite true that in the initial stages of the growth of silicon crystals twinning often starts from slag, either present on the surface or introduced with the seed, once the technique has been mastered this is a rare occurrence. When changing the conditions of growth, however, with regard to temperature or speed, we have seen striking examples from time to time of twins evidently due to stress of some kind. Notably in the growing of crystals in the [111] orientation, twinning often starts simultaneously on the three typical facets spaced 120° apart, and with the same twinning plane, about 30° inclined to the growth axis. It seems to me improbable that such symmetry could arise from insoluble impurities, which are presumably randomly distributed

particularly as the onset of these twins under identical growing conditions always occurs after the same length of crystal has been produced. The nature of the stress giving rise to the effect must be a matter of speculation. It could be a mechanical shear force, or a thermal stress, or a combination of both.

Dr. CHURCHMAN (*in reply*): I would thank Mr. Madsen for his comments regarding mechanisms for thermal detwinning. Whilst I have not observed the growth of recrystallized grains preferentially along the path of twins in titanium, I have done so in another hexagonal metal, rhenium. It is possible that both the suggested mechanisms are operative in thermal detwinning. The predominant one would be determined by the strains associated with twins: the strains associated with the formation of mechanical twins are high in rhenium but apparently low in titanium, where the twin boundaries are more easily moved under stress. When the strains associated with the deformation twin are high, Madsen's mechanism is operative, but where, as is the case in titanium, the associated strains are low, the relative amount of deformation in the twin and matrix would be the governing factor.

Dr. BILLIG (*in reply*): In the practical pulling of silicon crystals, various types of defects can arise; how far they are avoided in any particular ingot is largely a question of skill.

The investigations described in the paper were carried out in an effort to clarify in detail the causes of several of the more commonly occurring defects in silicon. Nucleation by insoluble impurities and thermal stresses were discussed as the two most likely causes. In a recent experimental investigation, these two factors could be demonstrated to produce defects similar to those occasionally observed in commercially grown crystals.

A paper dealing fully with these investigations is about to be published.

Discussion

The Cleavage Fracture of Pure Polycrystalline Zinc in Tension

By G. W. GREENWOOD and PROFESSOR A. G. QUARRELL

(*Journal*, 1953-54, 82, 551)

Dr. P. L. PRATT,‡ B.Sc.: The authors are to be congratulated on their convincing demonstration that a dislocation theory can be developed to account for the existence of large internal stresses which result in cleavage. Furthermore, they have provided a natural interpretation of the transition temperature which accounts for the dependence of fracture strength upon strain rate and temperature.

I am a little worried, however, by the initial treatment of their material, since the unannealed specimens, cut from different parts of the extruded bar, might well be in varying states of prestrain compared with the annealed specimens. From the experimental results this would appear to be unimportant, but did the authors consider that the specimens were strictly comparable?

It is interesting to note that specimens deformed at -196° and at -160° C. showed prior twins crossing the path of the fracture. This means that the crack propagated discontinuously from twin to twin at these temperatures; if the twins were present before the pile-up of dislocations responsible for the first cleavage crack, the measured grain-size would be too large because the twins themselves would act as grain boundaries. However, the authors state that twins were confined to grains adjacent to the fracture surface, and from Fig. 15 of the paper (Plate LXXXVIII) it would

seem that the twins (all of one family) were created by the stress wave ahead of the cleavage crack after the crack had started to propagate. The point is of interest, since prior twinning can effectively convert a single crystal into a polycrystal of grain-size equal to the spacing of the twins from this aspect. Mr. W. D. Biggs, at Birmingham University, has shown that substitution of the measured twin spacing, found in single crystals of iron, into a formula of the Griffith type gives a surprisingly good agreement with the measured fracture stress.

The authors state that strains of >0.07 inhibit twinning, and in their photographs river-line markings appear on the cleavage surface. These markings are typical of deformed material, and are principally due to screw dislocations, introduced during the deformation, cutting through the cleavage plane. This point is best illustrated by considering the appearance of cleavage fracture surfaces after various treatments. The most perfect cleavage of calcite (Fig. A, Plate LXXXVIII) shows an almost flat surface extending from the start of the fracture most of the way across the specimen. A less perfect, and more common, type of fracture found on many undeformed crystals (Fig. C, Plate LXXXVIII) shows a system of steps radiating from the start of the fracture in such a way that these cleavage steps are orthogonal to the

* R. W. Cahn, *Acta Met.*, 1953, 1, 49.

† Transitron Electronic Corp., Melrose, Mass., U.S.A.;

formerly with Standard Telephones and Cables, Ltd., London.

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instantaneous position of the fracture front. With prior deformation on glide systems intersecting the plane of cleavage, the river-line pattern is found (Fig. B, Plate LXXVIII) with steps arising over the whole fracture surface and converging in the direction of crack propagation. The effect of dislocations remaining in the material after deformation is primarily to work-harden it, but screw dislocations may be responsible for the inhibition of twinning, and they certainly make it harder for cracks to propagate, because additional surface energy has to be applied to form the new steps on the surface. Sufficient prior strain (>0.3) then makes it impossible for a crack to propagate at all, and the material gives a ductile fracture. This is confirmed by the specimen shown in Fig. 14 of the paper (Plate LXXXVIII), in which cleavage did occur, but not in the deformed region of highest applied stress. The decrease in σ_c with prior strains from 0.05 to 0.3 may be due to the lack of twins, as the authors suggest, or it may be that the prior deformation uses up dislocation sources in the material, so that large pile-ups will occur more readily in the harder material without local relaxations.

Dislocation theories of fracture assume that about 10^3 dislocations must be stopped at a barrier to create the magnified normal stress. Now, pile-ups of about ten dislocations only are sufficient to activate new sources of slip near the pile-up in annealed material, so that these sources must be prevented from acting before 10^3 dislocations can be stopped. Prior deformation, as indicated above, may exhaust these sources; other than this, only rapid rates of strain and impurity atoms can lock the sources, and the effectiveness of impurity atoms increases with decreasing temperature. This subtle effect of impurity atoms seems to provide a possible explanation of the brittle behaviour of the authors' material, since zinc of only 99.99% purity was used, and while it exhibited no yield point it did show jerky flow associated with strain-ageing. Zone-refined material might show a much lower transition temperature, since locking of the dislocation sources by impurity atoms, and hence large pile-ups, should not occur.

Dr. G. B. GREENOUGH,* M.A. (Member): The explanation put forward by Dr. Greenwood and Professor Quarrell of low value of the stresses necessary to cause cleavage fracture is in terms of stress concentrations near the head of dislocation pile-ups. Extremely good numerical agreement is obtained between the calculated magnified tensile stress and the theoretical strength of zinc, and the correct relation between grain-size and fracture stress is predicted. It therefore seems clear that the theory must be somewhere near the truth.

The difficulty in the theory is that the plane of the maximum magnified tensile stress is at 70° to the slip plane,[†] and the component of the magnified stress across the slip plane is zero. In zinc, where the slip plane and cleavage plane coincide, the stress concentration near a dislocation pile-up in a grain seems unlikely to produce cleavage in that grain. In polycrystalline material, which the authors examined, this may not be a serious objection, since a dislocation pile-up at a grain boundary will produce a stress concentration in the next grain. This could well be so orientated that the magnified tensile stress was across the cleavage plane. But single crystals cleave at stresses comparable with the polycrystalline material, and here there appears to be no obvious way out of the dilemma.

An alternative approach to that involving magnified stresses may lie in energy considerations. The original theoretical treatment of fracture due to Griffith was that a crack of critical size would just propagate if the decrease in the elastic strain energy in the material near the crack equalled the increase in surface energy of the crack. This led to the concept of the Griffith-crack size, which appears to be impossibly large for metals. But dislocations are associated with elastic energy and, in particular, the strain

energy associated with a dislocation pile-up is high. It may be, then, that the criterion for the initiation of cleavage fracture is that the dislocation strain energy in a small region at the head of a pile-up must exceed the surface energy of a crack along the slip plane in the same region. This then propagates along the pile-up and the remaining dislocations provide some of the energy required for its propagation. A detailed treatment of this idea yields the same laws for polycrystalline material as those deduced by the authors, with the same sort of numerical agreement. Its main advantage is that it can be applied to single crystals.

This idea springs from many discussions in this Department and, in particular, owes much to Mr. R. Bullough, who first pointed out that the bubble model indicates that cohesion across a slip plane appears to be reduced by dislocations on the slip plane.

A further point on which the authors' comments would be interesting is the possible influence on the measured fracture stresses of stresses arising from the thermal anisotropy of zinc. If the grains were stress-free at room temperature then, assuming no plastic deformation during cooling, tensile stresses of up to 40 tons/in.² perpendicular to the cleavage plane would be present at -196°C . in some grains. This is greater than the observed fracture stresses.

If the authors' theory is correct, however, the important stress is the shear stress across the slip plane. For a single anisotropic grain in an isotropic matrix, there is no contribution from the thermal stresses to this shear stress. But if the grain under consideration is surrounded by other anisotropic grains, there will be a small thermal shear-stress component across the slip plane. This may help or hinder the applied stress in causing fracture in different grains, but since the fracture of one grain is sufficient to initiate the complete fracture of the aggregate, it seems likely that the largest combined stress is important. Thus, stresses due to thermal anisotropy will lower the applied stress necessary to cause fracture, the effect being the greater the lower the temperature.

Could this be the explanation of the observed reduction of fracture stress with temperature, which is otherwise somewhat unexpected?

Dr. GREENWOOD and Professor QUARRELL (*in reply*): We are pleased to find Dr. Pratt and Dr. Greenough substantially in agreement with the chief conclusions of our paper, and we are grateful to them for presenting additional comments in the interpretation of the results.

Dr. Pratt's detailed account of the relation of deformation and fracture provides a useful supplement to the paper. Since twinning was entirely in grains adjacent to the fracture surface of our specimens, there seems no doubt that dislocation pile-up could occur on slip lines extending across whole grain diameters, twins being formed just ahead of the advancing crack. In iron single crystals, if twinning occurs throughout the specimen before fracture, then the length of slip line available for dislocation pile-up may be expected to be equal to the measured twin spacing. With regard to the decrease of σ of our specimens with prior deformation from 0.05 to 0.30, we merely suggested that this may be connected with lack of twinning.

Impurity atoms may have the effect of locking dislocation sources and preventing stress relaxation. This point is worth further investigation, using materials of extremely high purity. In our experiments two varieties of zinc were studied, having slightly different analyses, but both showed strain-ageing and gave identical experimental results.

Dr. Greenough raises the question of the effects of internal stresses in our specimens due to thermal anisotropy. Tensile stresses perpendicular to the slip plane up to the magnitude he has calculated may possibly be present, though the value may be reduced considerably by plastic deformation. Moreover, the resultant shear-stress component across the slip plane

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† A. N. Stroh, *Proc. Roy. Soc.*, 1954, [A], 223, 404.

arises only because the grain under consideration is surrounded by anisotropic grains and the magnitude of this shear stress is probably negligibly small. Dr. Greenough suggests that the internal stresses due to thermal anisotropy may account for the rise in σ with temperature. If the suggestion is correct, a more complex relation between σ and grain-size might have been looked for, since the internal stresses would be expected to superimpose an effect independent of grain-size. The fact that the shear-stress component along the slip planes due to thermal anisotropy is probably small, may be the reason why comparable results were obtained from annealed specimens and from specimens cut from extruded bars.

Dr. Greenough considers that the chief difficulty in the dislocation theory of cleavage as presented in the paper lies in its possible application to results on zinc single crystals, where it is necessary to explain the low cleavage stress when the slip plane is also the cleavage plane. Though his statement that

the maximum tensile-stress magnification for piled-up dislocations occurs across a plane about 70° to the slip plane is correct, it is not true that there is no tensile-stress magnification in a direction perpendicular to the slip plane. Dr. Greenough suggests that the dislocation theory presented does not allow a stress magnification perpendicular to the slip plane, but that a potential treatment of the problem by energy considerations of piled-up dislocations indicates a weakening of cohesion across the slip plane. He states further that the results from the alternative theory agree equally well with experimental results on polycrystals. It appears that his alternative theory is in essence similar to the one presented in the paper. Whether the effects of a group of piled-up dislocations are considered in terms of stress magnification or of weakening of cohesion is not a major consideration. Refinements of the theory must depend on more detailed calculation of stress and energy distributions.

Discussion

The Constitution of Uranium Alloys *

Dr. W. HUME-ROTHERY,† O.B.E., F.R.S. (Member): It is satisfactory to know that we have reached the stage when open discussion of research work on the constitution of uranium alloys is permitted. Papers submitted show the different lines of approach adopted by four laboratories, and the ingenuity of some of the experimental methods and apparatus is noteworthy. The following comments may be offered on the papers under discussion.

The uranium-zirconium equilibrium diagram is of a most interesting type, and it is to be hoped that the theoretical physicists will examine the formation of the ($\gamma_1 + \gamma_2$) miscibility gap. It is not, however, clear exactly what was being measured in the methods for liquidus determinations described on p. 278 of the paper by Dr. Summers-Smith. With a pure metal, or an alloy which freezes at constant temperature, the interface between the small pool of liquid and the solid portion of the alloy in the arc furnace should be at the true freezing point, and the method described should be accurate. Where, however, the alloy melts over a range of temperature, equilibrium conditions require the liquid and solid phases to be of different compositions when in equilibrium at a given temperature, and it would seem that the author's method might give any temperature between the liquidus and the solidus. Perhaps also Dr. Summers-Smith would make clear what exactly is the difference between the measured and calculated temperatures in Table I (p. 280). Are the calculated temperatures those deduced by some theory, or are they the observed temperatures corrected for absorption and non-black-body conditions?

The two papers from Harwell are of extreme interest and show the enthusiasm of the authors for this kind of work, but protest may be made against the unduly small scale on which some of the diagrams have been reproduced, since in some cases this prevents the details being appreciated easily. This criticism is, of course, not directed towards the authors, but to the Institute's arrangements for publication.

In the work on the system uranium-lead Dr. Frost and Mr. Maskrey describe a hot centrifuge for separation of solid and liquid, but they have apparently ignored the results obtained with this apparatus, and it would be interesting to know whether it proved satisfactory or not. At the lead-rich end of the diagram, the form of the liquidus is such that thermal analysis is unlikely to be accurate, but it is not

clear why the authors did not adopt the relatively simple method of maintaining a partly liquid alloy at constant temperature and allowing the solid phase to float to the top or sink to the bottom according to its relative density. This method has been employed in many other cases, and unless the densities of solid and liquid are nearly the same, centrifuging appears unnecessarily elaborate.

The authors also raise the question of the UX_3 compounds with the $AuCu_3$ type of structure, and here it may be suggested that the same structure may be formed for two quite different reasons. In the $AuCu_3$ superlattice structure the formation of the ordered arrangement prevents two relatively large gold atoms from being nearest neighbours, and thus relieves lattice strain which would be present in a random solid solution. This principle is well established for many superlattices. In the above case the fact that gold atoms keep as far away from one another as possible naturally results in each gold atom having a maximum number of copper atoms. If we then have a compound AB_3 in which there is something like real chemical combination between A and B atoms, this may result in each A atom surrounding itself with the maximum number of B atoms. In such a case the A atoms will naturally be kept away from one another, but this will not be due to a tendency to relieve the strain of a random arrangement. In this way we can understand why the same type of structure may be formed for quite different reasons. The type of diagram shown in Fig. 9 (p. 176 of the paper) obviously suggests strong combination between the two metals, because the solid compounds extend to temperatures far above those expected if the melting points of the two metals are joined by a straight line.

In the paper on the uranium-mercury system by Dr. Frost, criticism may be made of the statement on p. 462 that: "Where several compounds are formed in a system, the compound having the highest melting point is obviously the one in which the electrochemical factor has its maximum effect." For reasonable comparison, one must surely consider the composition and the relative melting points of the two metals? If, for example, two metals A and B have melting points of 200° and 1200° C., respectively, a compound A_4B melting at 700° C. will have a melting point 300° C. above that corresponding to a straight line joining the values for the pure metals A and B in the equilibrium diagram. This

* Joint discussion on the following papers published in the *Journal*: J. D. Grogan and R. J. Pleasance (with an appendix by B. E. Williams) (1953-54, 82, 141); B. R. T. Frost and J. T. Maskrey (1953-54, 82, 171); B. R. T. Frost (1953-54, 82, 456); G. B. Brook, G. I. Williams, and (Mrs.)

E. M. Smith (this vol., p. 271); D. Summers-Smith (this vol., p. 277).

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will surely suggest a higher electrochemical factor than in a compound AB_4 melting at 800°C ., this temperature being 200°C . below a linear relation.

The paper by Mr. Brook, Dr. Williams, and Mrs. Smith raises the question of the cause of the formation of the Laves phases. The tendency to regard these phases as resulting from a particular radius ratio is not always convincing, particularly when, as the authors explain, the ideal ratio is 1.225 and is replaced by actual ratios varying from about 1.1 to 1.6. When the Laves phases are examined it is found that whereas the large atoms A are always so arranged as to form tetrahedral bonds between themselves, the arrangements of the small atoms B vary in the different structures. May it not therefore be possible that the real cause of the structure is the tendency of the large atoms to form tetrahedral bonds? This view is perhaps confirmed by the fact that in the list of these compounds given by Berry and Raynor* there are more examples in which the A element is from Group IV than from any other Group. If this view is correct, the cause of the structure is the tetrahedral bonding, and this naturally imposes restrictions on the sizes of the interstices to be filled by the remaining atoms. If it is asked why an element such as titanium in Group IV does not form the diamond structure, it may be suggested† that this is because the diamond structure contains too much empty space to be stable, but that if one fills some of the space with smaller atoms, as in Cr_3Ti , then the tetrahedral bonding is possible. It must be emphasized that this view would not restrict the formation of these compounds to A elements of Group IV—thus even the alkali metals form 4-covalent organic compounds.

In the work on the uranium-nickel system it would seem that further investigation is needed before the part of the diagram between 50 and 85 at.-% nickel is established. It would be helpful if Mr. Grogan and Mr. Pleasance would say whether any examination was made of the interplanar spacings of the compounds given in Table II (p. 147 of the paper). Presumably some attempt was made to index the lines and even negative information might help later workers.

Dr. A. D. McQUILLAN,‡ B.Sc. (Member): The difficulties experienced by various authors in attempting an explanation of the form of the constitutional diagrams of uranium with other transition elements in terms of the simple concepts shown to apply to many of the binary systems of non-transition elements, would seem to have made it abundantly clear that this approach is not likely to be fruitful. If we examine the physical properties of the earlier transition elements of each period, and more especially the variation of such properties as resistivity, thermoelectric power, magnetic susceptibility, and Hall coefficient with temperature, it is clear that the elements uranium, plutonium, titanium, zirconium, and others of Groups IVA, VA, and VIA of the Periodic Table of the elements, behave in a manner quite incompatible with the assumption that the electrons in these metals can be treated as free electrons. Similarly, the properties of the solid solutions based on these elements show marked deviations from the type of behaviour to be expected of normal binary solid solutions. The recently published results of Mr. Ames and myself§ on the resistivity/temperature/concentration relationships in the β phase of the titanium-niobium system, illustrate that the electrical properties of single-phase alloys are quite inexplicable in terms of a free-electron model. I would suggest that measurements of the resistivity/temperature/concentration relationships of γ -phase uranium-rich alloys would show that a similar situation exists in these elements.

At the present moment, there would seem to be two possible mechanisms which might be used to explain the unusual

properties of these materials. There is the possibility, for example, of thermally activated transitions occurring between different electronic states requiring activation energies of less than 1 eV. Such changes would have the effect of altering the form of the electronic bonding as the temperature, and very probably as the concentration of addition elements, is increased. This type of behaviour has already been suggested as an explanation for some of the properties observed in titanium-chromium alloys.|| The second possibility is that we are dealing with effects due to Brillouin zones of higher order than the first, and that in the case of elements with an even number of bonding electrons per atom the electrons lie in an almost full band. If this were true, then the conduction electrons could not be regarded as free electrons, but would behave in a manner characteristic of electrons with a very low effective mass which might have either a positive or a negative value. An investigation of the effect of temperature and amount of addition element on the Hall coefficient of the materials would therefore probably yield fruitful results.

A knowledge of the form of the constitutional diagrams, although a necessary prerequisite for the study of the alloying behaviour of the transition elements, will, in my opinion, give us little insight into the nature of the electronic bonding in the materials unless this is combined with a detailed and accurate knowledge of the physical properties of each individual phase. I would suggest, therefore, that the time has now come for a greater effort to be made to collect the necessary data on the physical properties.

In the absence of any knowledge of the type of bonding existing in uranium and associated elements, it is not surprising that all attempts to explain the crystallographic form of the multiplicity of phases which exist in the systems of uranium with the transition elements have so far proved unsuccessful. In fact, the mere existence of such large numbers of phases of closely similar compositions would strongly suggest that the stability of the phases is not greatly dependent on crystal structure.

Mrs. M. K. McQUILLAN,¶ M.A. (Member): A number of features have been observed in binary uranium systems for which explanations are required, among them the (γ_1 - γ_2) miscibility gap in the uranium-zirconium system and the disputed existence of the compound UZr_2 . Before seeking explanations of specific phenomena, however, there may be some advantage in looking at the problem more generally. For instance, the miscibility gap is a feature common to the uranium-zirconium, uranium-titanium, uranium-niobium, and titanium-chromium systems. Thus, the problem is not one associated with any individual element or even with any particular group of the Periodic Table. The greatest limitation which we can safely impose is probably to say that we are dealing with the early transition elements, i.e. those forming Groups IVA, VA, and VIA, a significant feature of which is that they all form body-centred cubic lattices; and it is possible that a general study of the body-centred cubic solid solutions will help to resolve many of the anomalies observed in the binary alloy systems.

Among the anomalous features of the titanium-chromium system which appear to be associated with the behaviour of the body-centred cubic solid solution, is the precipitation of the compound TiCr_2 during quenching. In some instances the quenching rate necessary to prevent the precipitation of TiCr_2 is both rapid and critical, and it is difficult to draw safe conclusions from the microstructures of such alloys after quenching. Is it possible that behaviour of this kind is contributing to the difficulties experienced in the study of uranium alloys?

* R. L. Berry and G. V. Raynor, *Acta Cryst.*, 1953, **6**, 178.

† I owe this suggestion to Mr. H. M. Powell, F.R.S.

‡ Department of Physical Metallurgy, University of Birmingham.

§ S. L. Ames and A. D. McQuillan, *Acta Met.*, 1954, **2**, 831.

|| M. K. McQuillan, *J. Inst. Metals*, 1953-54, **82**, 433.

¶ Imperial Chemical Industries, Ltd., Metals Division, Birmingham.

Dr. M. B. WALDRON,* B.Sc., A.I.M. (Member): It is interesting to learn Dr. McQuillan's views on the transition-metal systems with which the papers by Grogan and Pleasance and by Brook, Williams, and Smith are concerned. Whilst I agree with him that there are general trends in these systems which hint at a systematic explanation of what is transpiring, I feel it is too naïve to suggest that as one passes through the sequences of binary systems from uranium-chromium to uranium-copper the stability of the compounds moves away from the uranium-rich end.

The melting points of the two types of compound that are common to four of these systems are tabulated below, together with approximate melting points of the pure transition metals. It will be seen that the melting points of the compounds in each case follow the trend of the melting points of the pure metals, except that the uranium-rich U_6X series has a maximum stability centred on cobalt, while the UX_2 series has its maximum centred on iron, in contrast with the general deduction expressed by Dr. McQuillan:

Melting Point, °C.			
X	Metal	U_6X	UX_2
Mn	1240	730	1125
Fe	1535	805	1230
Co	1490	830	1190
Ni	1455	790	985

These figures might be regarded as suggesting that the uranium atom in each series does not greatly vary in its electronic contribution along each series, though this is not necessarily the same in both cases. In support of this, the atomic volumes are more or less additive in these compounds, with a slight negative discrepancy on moving from manganese to nickel. It still seems to me that one has to explain in some more precise way the additional compounds formed in the uranium-cobalt and uranium-nickel systems.

The view has been advanced that the details of the compounds formed are unimportant; where there are many compounds, it is suggested that the atoms just do not mind much how they arrange themselves. One is still left wondering why UCO_2 has a wide solubility for cobalt in the binary system, and yet in the nickel system, which contains the greater number of compounds, there is very little range of solubility in either UNi_2 or the very similar UNi_6 . I suspect that the extensive solubility in UCO_2 is connected specifically with cobalt, since Fig. 1 (p. 273) of the paper by Mr. Brook and his co-authors shows that the T -compound in the cobalt-nickel series has a wide range of homogeneity that embraces the two restricted compositions of the T -phase in the manganese-nickel and iron-nickel systems.

The UX_2 Laves phases were examined in detail at the Fulmer Research Institute, as being relatively simple types of compounds which have been studied extensively in non-uranium systems. Since the ratio of atomic diameters is not far removed in each case from 1.225, it was thought possible that effects similar to those found in other Laves phases might apply and thus give some understanding of compound formation in uranium alloys. The magic numbers which Dr. Pfeil and I produced, which are referred to in the discussion section (p. 276) of the paper, were arrived at on the basis of three assumptions recognized as being quite arbitrary at the time: (a) that the electron:atom ratio of 1.8 still characterized the change from the $C15$ $MgCu_2$ -type to the $C14$ $MgZn_2$ -type structure in all the transition-metal systems with gadolinium, titanium, zirconium, niobium, or tantalum; (b) that the transition metals exerted the same valencies

throughout; and (c) that the other elements, including uranium, exerted the same valencies throughout. The valency of 2 for uranium and the particular fractional valencies deduced for the transition metals have no other specific experimental or theoretical support. The Pauling approach leads in fact to large valencies for both uranium and the transition metals in these compounds. The values deduced by Brook and his colleagues of 0.65, 0.74, and 0.85 are sufficiently different from those deduced by us to mean that one or more of our assumptions was not justified. This does not surprise me!

It has been questioned why UNi_2 should have a $MgZn_2$ -type structure rather than UMn_2 , which has the greater deviation from the ideal atomic diameter ratio (w ideal). As I understand Berry and Raynor,† their conclusion was that in any series of this kind, there was a band of w values, more or less around w ideal, which was associated with the $MgCu_2$ structure. The significant point is that UNi_2 should be at one end of the range of w -values. Raynor‡ has also suggested, for the magnesium-bearing compounds, that the $MgNi_2$ structure ($C36$) is a more or less convenient "half-way house" from the $C15$ to the $C14$ structure. The haphazard compositions of the T phases in Fig. 1 of the paper by Brook *et al.* would be in agreement with this.

Dr. H. J. AXON,§ B.Met. (Member): I should like to comment on Table VI (p. 178) of the paper by Dr. Frost and Mr. Maskrey on the uranium-lead system. In column 4 there appear to be two misprints, namely the $U-X$ and $X-X$ distances in the compounds UGa_3 and UPb_3 which, it seems, ought to have the values 3.002 and 3.38 Å., respectively.

In this table the authors have tried to correlate the measured and theoretical interatomic distances in the compounds of uranium with the trivalent elements aluminium, gallium, and indium, and with the quadrivalent elements silicon, germanium, tin, and lead. In attempting such a correlation much depends upon the values chosen to represent the effective sizes of the various atomic species, including uranium itself. My contribution to the discussion represents a tentative effort to evaluate a set of atomic diameters for the pure elements more self-consistent than the values given in column 5 of Table VI and more realistic than the value of 3.00 Å. widely used for the effective size of the uranium atom in metallic structures. It must be stressed that the values for the effective sizes of the atoms presented below are designed to apply to the particular case of the face-centred cubic structures listed in Table VI of the paper and do not necessarily apply to other structures. The common feature of these compounds is an ordered f.c.c. structure for which the co-ordination number is 12; hence it may first be desirable to evaluate the effective atomic diameter of each element for co-ordination number 12.

For aluminium and lead the closest distance of approach of atoms in the pure elements would be expected to serve; these values are 2.85 and 3.49 Å., respectively. The value of 2.75 Å. used for aluminium in Table VI appears to approximate to its effective size in a b.c.c. rather than in a f.c.c. structure.

For silicon, germanium, and gallium the effective atomic diameters for co-ordination number 12 are given by Hume-Rothery and Raynor¶ as 2.67, 2.79, and ~2.7 Å., respectively; these would appear to be the most reasonable values for use in discussing the interatomic distances in the compounds. Face-centred tetragonal indium approximates to face-centred cubic, and the closest distance of approach, 3.24 Å., may reasonably be taken. White tin is often regarded

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† R. L. Berry and G. V. Raynor, *Acta Cryst.*, 1953, 6, 178.

‡ G. V. Raynor "Progress in Metal Physics", Vol. I, p. 37. 1949: London (Butterworths Scientific Publications).

§ Senior Lecturer in Metallurgy, University of Manchester.

|| W. Hume-Rothery, "The Structure of Metals and Alloys", 2nd edn., 1944, p. 41.

¶ W. Hume-Rothery and G. V. Raynor, "The Structure of Metals and Alloys", 3rd edn., 1954, Tables V and VI, pp. 89, 90.

as a highly distorted diamond structure, of co-ordination number 4, and it may be permissible to add 12% to the closest distance of approach, giving a value of ~ 3.36 Å. for tin with co-ordination number 12.

Uranium itself presents a particular problem. Hitherto a value of 3.0 Å. has been taken for use in alloy theory, but this applies to b.c.c. γ -uranium, which is stable above 775°C ., and is obtained by the back extrapolation to zero molybdenum of the lattice spacings of uranium-molybdenum alloys. Apart from any uncertainty in the extrapolation, this gives a value for the uranium atom in a structure of co-ordination number 8. The atomic diameter in α -uranium is generally ignored on the grounds that the structure is only "pseudo-metallic", but in the present series of compounds several of the elements associated with uranium are pseudo- or non-metallic, and it might be reasonable to evaluate an atomic diameter for α -uranium for use in discussing them. Estimates of its effective atomic diameter may be reached by two methods, both giving a value of ~ 3.14 Å. In the first method we may take the mean interatomic distance of the twelve nearest neighbours. In the second method we may consider the presence of two neighbours at 2.76 Å. and two at 2.85 Å. as being equivalent to four close neighbours at about 2.8 Å., and apply a 12% expansion to this in order to correct the atomic diameter from co-ordination number 4 to co-ordination number 12.

If 3.14 Å. is taken as the effective atomic diameter of α -uranium for co-ordination number 12, together with the values for aluminium, gallium, indium, silicon, germanium, tin, and lead suggested above, we may use these effective atomic diameters for co-ordination number 12 to calculate the interatomic distances in the uranium compounds. This is done in Table A, where it can be seen that there is excellent

TABLE A.—*U-X Distances Using the Effective Atomic Diameters for Co-ordination Number 12.*

Compound	U-X Distance, Å.		Discrepancy, Å.	Discrepancy using Frost & Maskrey's Values, Å.
	Calculated	Measured		
UAl ₃ . . .	2.995	3.01	0.02	0.09
UGa ₃ . . .	2.92	3.002	0.08	0.14
UIn ₃ . . .	3.19	3.25	0.06	0.13
USi ₃ . . .	2.90	2.85	-0.05	0.18
UGe ₃ . . .	2.96	2.97	0.01	0.25
USn ₃ . . .	3.25	3.27	0.02	0.27
UPb ₃ . . .	3.31	3.38	0.07	0.13

agreement between the measured and calculated interatomic distances in these compounds, if allowance is made for the variation of effective atomic size with co-ordination number and if the atomic diameter of α -uranium is taken. It would seem, therefore, that the series of compounds considered by Dr. Frost and Mr. Maskrey provide no unambiguous support for either contraction or expansion when the compounds are formed from the elements.

Mr. A. PRINCE,* B.Met., A.I.M. (Junior Member): I should like to bring to the attention of Dr. Frost and Mr. Maskrey a paper by Iandelli and Ferro,† in which values for the cell constants for a series of uranium compounds, including UPb₃, were given. The Italian workers examined uranium-thallium alloys and found an analogous compound, UTl₃, in this system. Their results are compared with those of Dr. Frost and Mr. Maskrey in Table B.

TABLE B.—*Comparison of Cell Constant Values in UX₃ Compounds.*

Compound	Cell Side <i>a</i> , Å.	
	Iandelli and Ferro	Frost and Maskrey (Table VI, p. 178)
UGa ₃	4.249	4.2475
UIn ₃	4.588	4.601 ₃
USi ₃	4.034	4.035 ₃
UGe ₃	4.198	4.206 ₂
UPb ₃	4.737	4.783 ₄
UTl ₃	4.675	...

Dr. A. G. KNAFTON,‡ B.Sc. (Junior Member): Since the paper by Dr. Summers-Smith on the uranium-zirconium system was submitted, further work at the Associated Electrical Industries Research Laboratory has led to the view that an intermediate compound occurs in the system near 70 at.-% zirconium and at temperatures below 600°C .

The structure and phase relationships of this compound have not yet been determined in our work, but some observations on its behaviour have been made. X-ray powder and glancing-angle photographs taken from specimens given anneals of a few hours' duration below 600°C . show predominantly the compound pattern. Annealing of the powders causes decomposition of the compound into α -uranium and α -zirconium, and decomposition is observed at the edges of metallographic specimens annealed at low temperatures. It thus appears probable that progressive contamination of the powder specimens during heat-treatment is responsible for the decomposition of the compound, and that when phases are identified from powder photographs of specimens which have been given long anneals, α -uranium and α -zirconium will be found.

Dr. Sci. M. VAN LANCKER,§ F.I.M. (Member): The mathematical interpretation of equilibrium diagrams can provide information of considerable value to the metallurgist in understanding the behaviour of alloys in the solid state, particularly in extractive metallurgy. A generalized version of the laws of thermodynamics, extended to the equilibrium between two solid phases, has led to the formulation of certain theoretical principles which are capable of application to some of the alloy systems used in atomic-energy production, notably in connection with reactors (diffusion phenomena in zirconium sheaths, &c.).

The application of these principles indicates that the equilibrium at a moderately high temperature between such solid phases as $\beta/(\beta + \gamma)$ or $(\beta + \gamma)/\gamma$ in the uranium-zirconium system is defined not by the upper solubility curve $\gamma \rightleftharpoons (\beta + \gamma)$ alone, but by a combination of this upper curve with the lower curve $(\beta + \gamma) \rightleftharpoons \beta$. It is therefore necessary to introduce into the calculations the entropy, ΔS_i , of transformation of the pure undercooled solid phase (e.g. the allotropic form corresponding to β -uranium), as well as the difference between the specific heats of the two allotropic forms of the pure metal, although the latter factor exerts a smaller influence. ΔS_i must be determined with the greatest accuracy possible. This value permits of the mathematical combination of the upper and lower curves mentioned above and gives the allotropic constant, which should prove to be not smaller than the molar depression of the transformation points of the upper solubility curve. The results of the calculations outlined show that the accuracy of the experimental measurements on the uranium-zirconium system can be considerably improved upon, giving an entropy value of the $\alpha \rightarrow \beta$

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† A. Iandelli and R. Ferro, *Ann. Chim. (Rome)*, 1952, **42**, 598.

‡ Research Metallurgist, Associated Electrical Industries Research Laboratory, Aldermaston, Berks.

§ Consulting Metallurgist, Anvers, Belgium.

transformation on the zirconium-rich side of 3.48 cal./°C., as compared with an experimental value of 0.82 cal./°C. The same comment applies to the uranium-rich side investigated by Dr. Summers-Smith.

In applying atomic thermodynamics to the study of liquid/solid equilibria in a binary system, it is essential to know with great accuracy the entropy of fusion of both constituents, in order to arrive at correct values of the cryoscopic constant, which gives, in conjunction with the size-factor and other effects, the liquidus points near the origin, as well as the corresponding solidus points, the two values being combined in the same mathematical expression. This constitutes the law of thermodynamic compatibility which I advanced some time ago (1952) and which governs the equilibrium between solid and liquid at a given temperature. The general rule must be verified and confirmed in relation to each new alloy system studied.

As the atomic fraction of the solute increases, the characteristic curves for the system, termed entropy/interaction curves, may be plotted. These help in classifying the system under consideration, and it is then possible to calculate the forces of attraction and repulsion between the presumed constituent particles and relate these to the appearance of new phases. From these data it is then easy to draw activity/concentration curves along the liquidus. Intermetallic compounds formed can also be investigated thermodynamically. Here it is essential that cryoscopic measurements of the highest accuracy should be made in the immediate neighbourhood of the melting point of the pure compounds in order to assess the probable molecular behaviour of compounds, such as UNi_5 , which in thermodynamic studies may be regarded sometimes as solvent and sometimes as solute.

The uranium-rich side of the uranium-nickel diagram, as established by Mr. Grogan and Mr. Pleasance, shows good accuracy as far as the liquidus is concerned, but a revision of the solidus values seems necessary, since the entropy curves which result from them are thermodynamically impossible. On the nickel-rich side, the liquidus is too low, and calculations show that, if the diagram is correct as published, UNi_5 should exhibit molecular properties.

Similar remarks apply to the uranium-mercury diagram of Dr. Frost between 1133° and 772° C. The solidus values in that region are not thermodynamically justified, and this view is confirmed by the entropy curves. In the region from 665° to 772° C., the calculations become more complicated by reason of the introduction of the transformation energies, but it is obvious that the change in the partial free energy during the extraction of 1 g.-atom of β -uranium from the β solid solution must be supplemented by the change of partial free energy on transformation of β -uranium to γ -uranium in the undercooled state, then by that of the melting of undercooled γ -uranium, and finally by that of the introduction of undercooled γ -uranium into the melt at the liquidus composition. The sum of these partial energies must be nil.

In the uranium-lead system, as drawn by Dr. Frost and Mr. Maskrey, there seems to be thermodynamic incompatibility in the liquidus curve between 75 and 90 at.-% lead. Moreover, given the eutectic depression of 2° C., the calculated uranium content at the eutectic should be 0.33 at.-%. Finally the course of the liquidus on both sides of the compound UPb seems possible.

Dr. Frost (*in reply*): Since the paper on the system uranium-lead has attracted considerable comment, we will deal with these questions first. With regard to the use of the hot centrifuge, this apparatus was used to obtain a rapid (but not highly accurate) trace of the liquidus curve. More accurate results were subsequently obtained by the resistivity method and were used to plot the final curve. It is true that gravitational settling may be used to separate the solid and liquid components, but experience at Harwell has shown that the settling rate of 10 μ particles of UPb_3 in lead is fairly slow. To minimize the risk of oxidation, the settling time should be as short as possible, and this can best be achieved by use of the centrifuge.

The series of UX_3 compounds has attracted considerable comment. We became aware of the Italian results to which Mr. Prince refers a short while after our own results were published and have, in fact, been able to consult this paper. Except in the case of UPb_3 , agreement between the two sets of results is good. Even in the case of UPb_3 , the U-Pb distances for the two investigations are 3.38 Å. (ours) and 3.35 Å. We were interested to see that UTl_3 had been identified, as it completes the series of Group IIIB and IVB elements. We have recently prepared this compound at Harwell.

If, as Dr. Hume-Rothery suggests, the series of compounds assumes the ordered AuCu_3 -type structure to satisfy mutual attractions and attain a maximum co-ordination of the two types of atom, one would expect the atoms to be as close together as possible. However, it is probably misleading to carry out calculations using the "billiard ball" model for the atoms; in this type of structure the atoms will certainly not be spherical, although Dr. Axon, choosing his parameters carefully, certainly presents a good case to show that the atoms do almost touch. We thank him for pointing out two mistakes in Table VI (p. 178); the value for UGa_3 was a miscalculation and that for UPb_3 a misprint, we believe.

A point of controversy in this system is the existence of a miscibility gap. In the diagram drawn by Teitel, evidence for such a region is based on thermal analysis and on segregation behaviour. The latter is not a reliable indication of immiscibility, while the accuracy of thermal analysis at about 1200° C. is not usually of a high order. However, Teitel has now evidence on this part of the diagram which he hopes to publish in the near future, so the issue is at present undecided. We would like to retract the statement which we made on p. 179 on the presence of intermetallic compounds under a miscibility gap. The phenomenon is observed in the systems uranium-copper and calcium-cadmium, being confirmed in the case of the latter by some recent thermal-analysis experiments of our own. This does not alter the fact that a thermodynamic analysis of this type of behaviour would be very interesting.

Turning to the uranium-mercury system, we agree with Dr. Hume-Rothery's criticism that the statement that the compound with the highest melting point has the highest electrochemical factor is not necessarily true. Strictly speaking, one should compare free energies at a constant temperature, but in the absence of these data the values of heats of formation are a reasonable guide. Certainly the value R is not a good one for comparison, e.g. in the case of the uranium compounds UHg_4 is the one whose melting point deviates most from a straight line joining the melting points of uranium and mercury.

Some criticism has also been levelled at the use of electrochemical factors based on measurements on chlorides with ionic bonding. Two alternatives suggest themselves: a scale derived from e.m.f. measurements made to determine thermodynamic activities (or even the activity coefficients, in a case like this where mercury is common to all the systems), or else on the basis of Pauling electro-negativity values.

In the discussion of the structures of the compounds, we have again talked in terms of spherical atoms in attempting to assess the closeness of packing, which is a rather dubious assumption. Mr. Heal has pointed out to us that, since the evidence on the two possible structures for UHg_2 is inconclusive, equal weight should be given to both. He added that one might expect ordering in UHg_3 which could be detected by the appearance of superlattice lines if one used monochromatic radiation. Since the two elements have similar scattering factors for X-rays, these lines would be difficult to detect unless one used the absorption-edge technique, as for copper-zinc alloys.

Dr. SUMMERS-SMITH (*in reply*): As Dr. Hume-Rothery points out, the solid and liquid phases at the interface of a pool of liquid maintained on a solid bead of an alloy have different temperatures. Thus, he is quite correct in suggesting that the temperatures measured will not necessarily be true liquidus ones. It is interesting nonetheless that successive

measurements of the interface temperature, readings being made by approaching from the liquidus side, agreed to within $\pm 10^\circ \text{C}$. The values bracketing the solidus temperature, which I feel are less open to criticism, are considerably lower than the "liquidus" temperature at the one composition where both were measured. Thus, the reproducibility of measurement does not appear to be a result of a narrow temperature range of melting, but suggests that some fixed temperature, viz. the liquidus, was being measured.

The calculated liquidus temperature values given in Table I of the paper were derived from the measured ones by applying

a correction factor to allow for absorption and non-black-body conditions.

Mr. GROGAN and Mr. PLEASANCE (*in reply*): In reply to Dr. Hume-Rothery, we agree that more work would be necessary to establish the region 50–85 at.-% nickel with greater accuracy, but the paper does not claim to have established the composition of the compounds X, Y, U_5Ni_7 , and U_7Ni_9 more than approximately. Attempts were made, of course, to index the lines from these compounds by the usual methods, but without success.

PHOTOMICROGRAPHS OF URANIUM-TITANIUM ALLOYS.

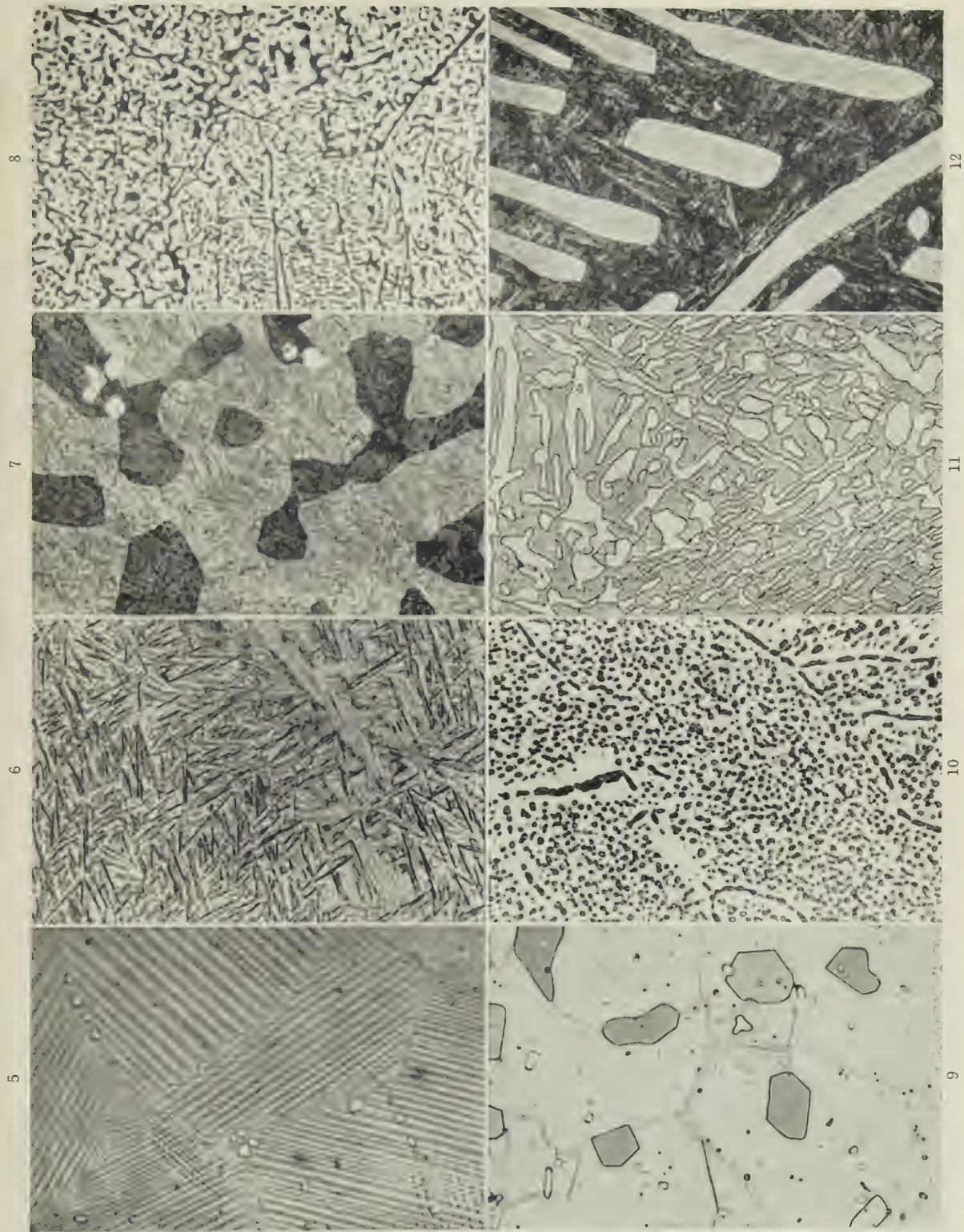


FIG. 5.—10 at.-% Titanium Alloy, Water-Quenched from 850° C. Transformed γ_2 showing banded structure. $\times 500$.
FIG. 6.—90 at.-% Titanium Alloy, Water-Quenched from 800° C. Transformed γ . $\times 400$.
FIG. 7.—4 at.-% Titanium Alloy, Water-Quenched from 740° C. Transformed γ (light) + transformed β (dark); oxide inclusions white. $\times 200$.
FIG. 8.—25 at.-% Titanium Alloy, Water-Quenched from 700° C. Unetched. Transformed β (dark) + ϵ . $\times 400$.
FIG. 9.—5 at.-% Titanium Alloy, Cold Rolled and Water-Quenched from 130° C. Transformed γ . $\times 400$.
FIG. 10.—60 at.-% Titanium Alloy, Water-Quenched from 850° C. ϵ (dark) + γ . $\times 500$.
FIG. 11.—20 at.-% Titanium Alloy, Water-Quenched from 850° C. ϵ (light) + transformed γ . $\times 400$.
FIG. 12.—99 at.-% Titanium Alloy, Water-Quenched from 850° C. δ (light) + transformed γ . $\times 400$.

MICROSTRUCTURES OF BINARY COPPER-ALUMINIUM ALLOYS ANNEALED AT 340° C.

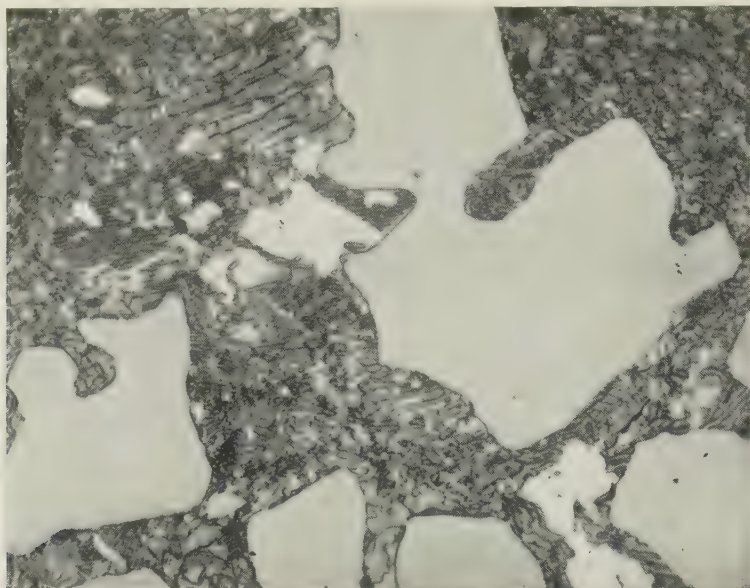


FIG. 1.—Alloy 4 Annealed for Approximately 6 Months at 340° C. The pink-etching phase is light, the γ_2 phase is half-tone, and the α is darker. $\times 800$.

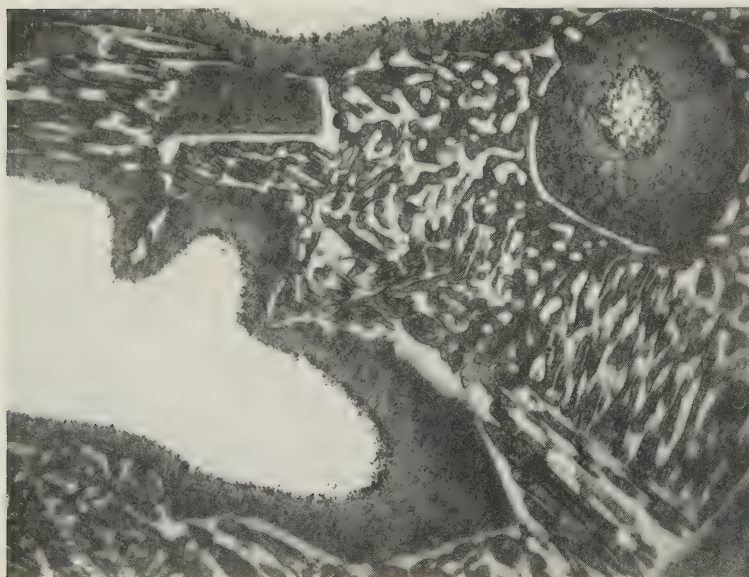
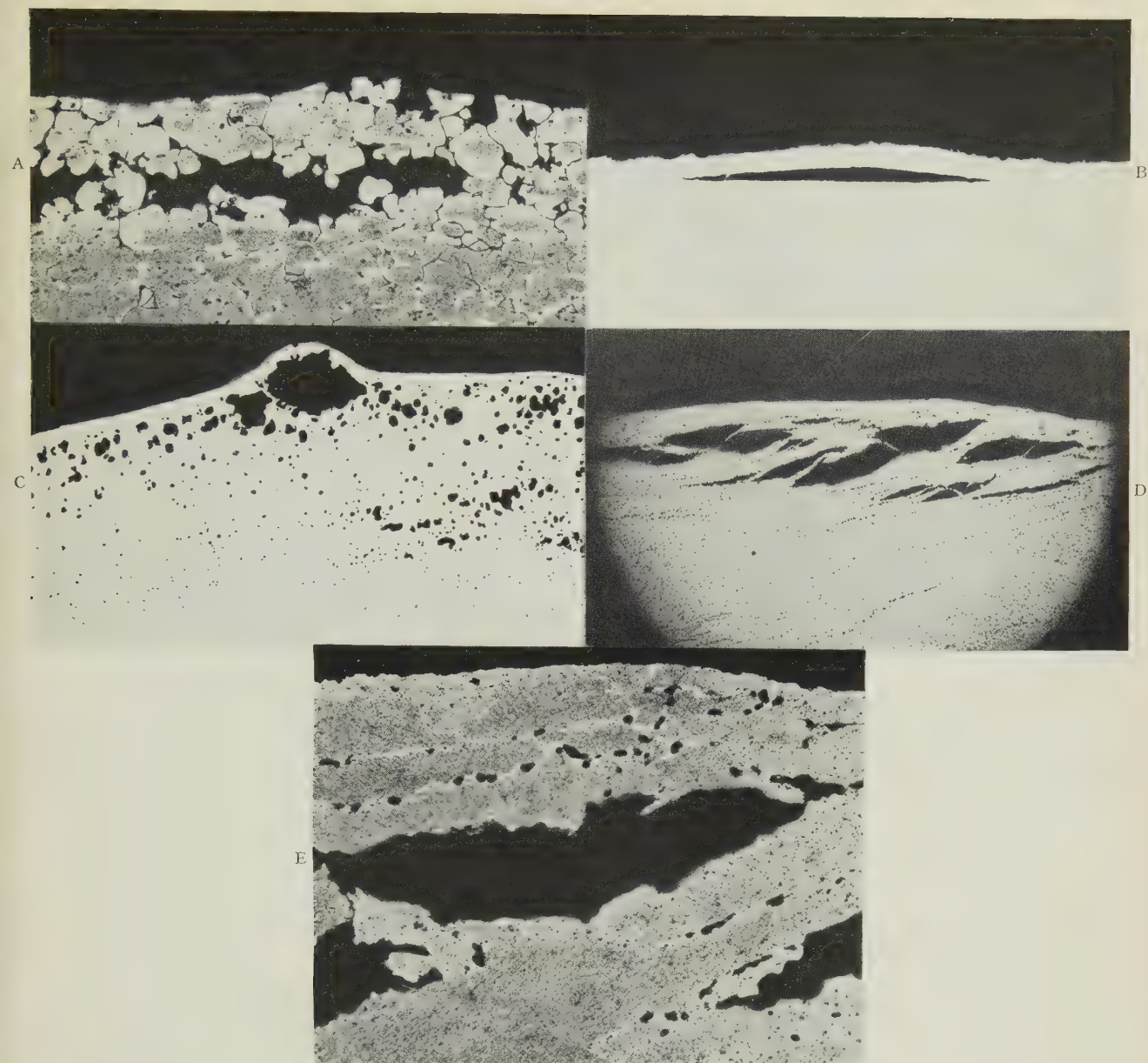


FIG. 2.—Alloy 2, Incompletely Stabilized at 520° C., and then Annealed for 6 Weeks at 340° C., Showing a "Coring" Effect in the Pro-Eutectoid α . The light particles in the eutectoid are the pink-etching phase. $\times 600$.

Etched in aqueous chromic acid solution.



FIGS. A-E.—Types of Blisters Encountered on Forgings Made from Extruded Stock in Certain Aluminium Alloys. (Chadwick.)

FIG. A.—Blister caused by overheating during solution-treatment. Etched in 25% HNO_3 at 70° C. for 4 min. $\times 100$.

FIG. B.—Blister of "double-skin" type in a heat-treated forging, caused by a defect in extruded stock. $\times 100$.

FIG. C.—Blister caused by reaction with furnace gases. $\times 100$.

FIG. D.—Blisters developed by heat-treatment and caused by insufficient lubrication during forging. $\times 100$.

FIG. E.—Forging showing evidence of overheating in the region of the blister caused by insufficient lubrication during forging. Etched in 25% HNO_3 at 70° C. for 4 min. $\times 150$.

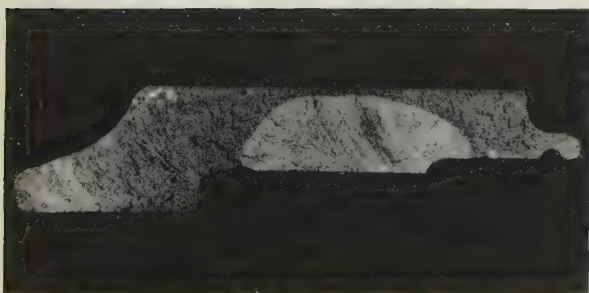


FIG. F.—"Flash-Line" Defect in Aluminium Alloy Forging. (Thorley.)

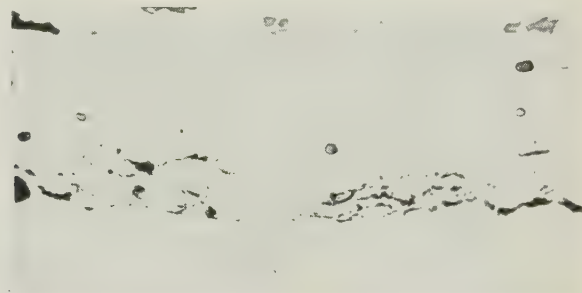


FIG. G.—Oxide Film on Aluminium Alloy Forging. $\times 1500$. (Thorley.)

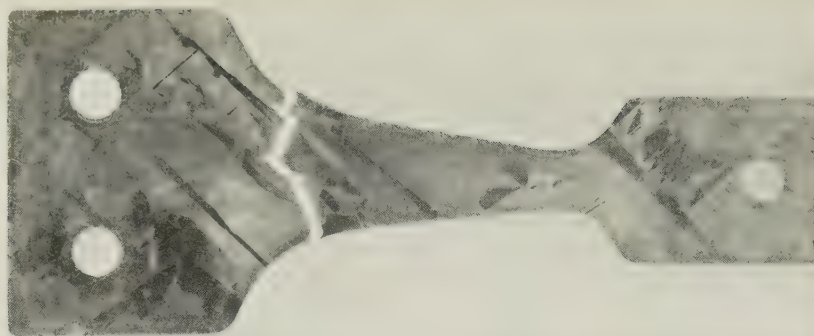


FIG. B.—Photomacrograph of a ruptured specimen. Etched in 30% HNO_3 before testing. $\times 1$.



FIG. C.—Photomicrograph of a ruptured specimen, showing inter- and intra-crystalline cracks. Etched in 30% HNO_3 before testing. $\times 20$.
(Reduced by $\frac{1}{4}$ in reproduction.)

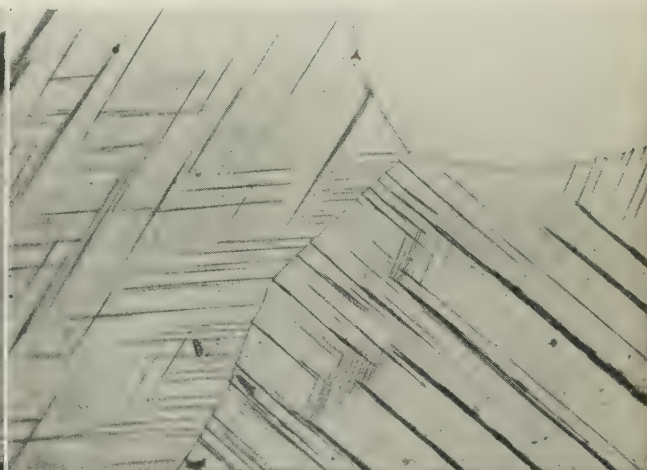


FIG. D.—Photomicrograph showing sliplines, slip bands, and striations in the neighbourhood of a crack. Electropolished in 50% H_3PO_4 before testing. $\times 125$.
(Reduced by $\frac{1}{4}$ in reproduction.)

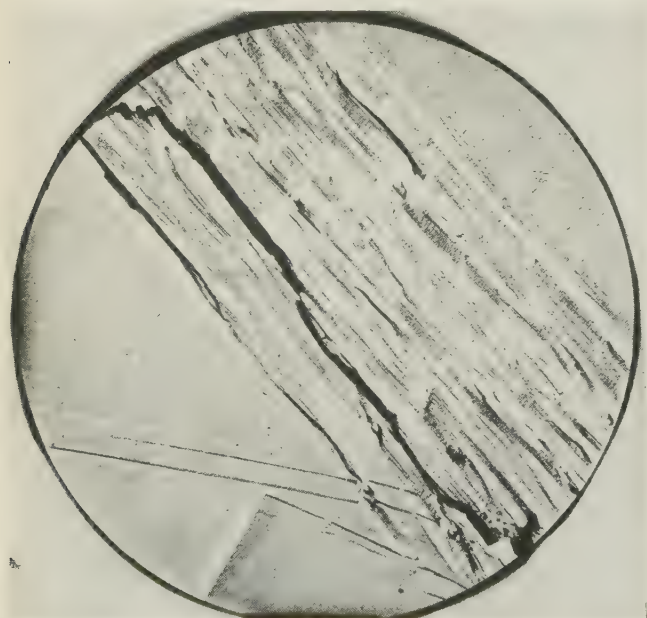


FIG. E.—Electron micrograph showing micro-cracks in a slip band in the neighbourhood of a macro-crack. Palladium-shadowed aluminium replica. $\times 5000$.

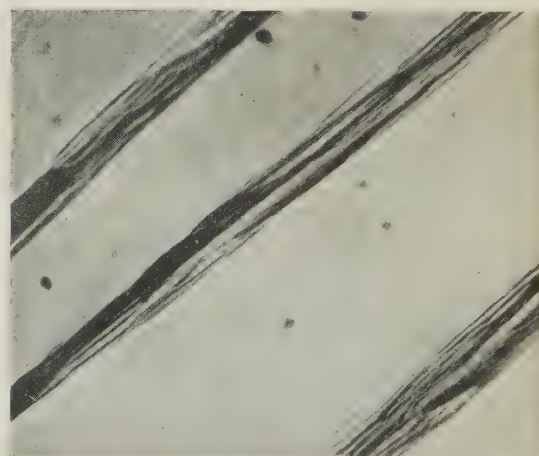


FIG. F.—Slip Bands in an Aluminium Crystal After 6% Elongation in Tension at 500°C . $\times 250$. (*Honeycombe*.)

FIGS. B-E.—Specimens of Coarse-Grained O.F.H.C. Copper After 100,000–200,000 Reversals in Bending. (*Ström*.)

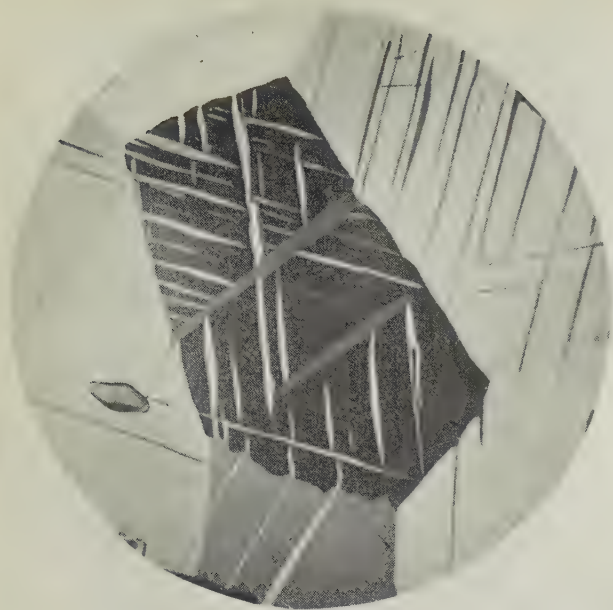


FIG. A.—Uranium Specimen Showing Migration of Intersections of Twin and Grain Boundaries Along Twin Boundaries on Annealing. Polarized light. $\times 1200$. (Madsen.)

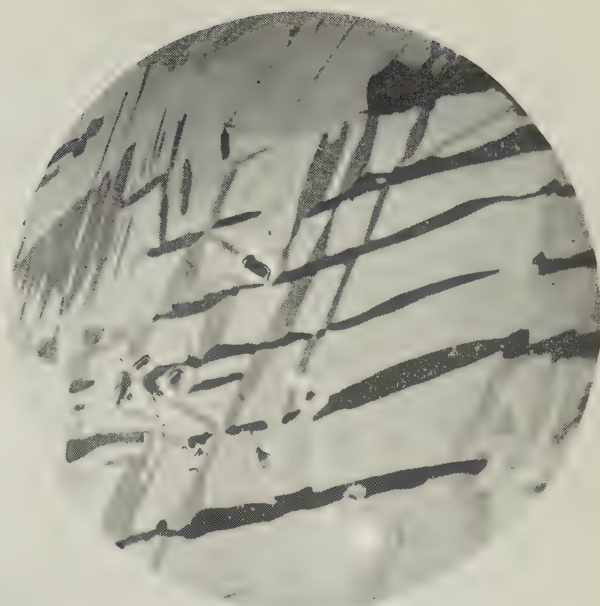


FIG. B.—Uranium Specimen Showing Growth of Intersecting Type-{172} Twins on Annealing. Polarized light. $\times 1200$. (Madsen.)

(Reduced by $\frac{1}{8}$ in reproduction.)

Discussion on Deformation and Fracture of Zinc

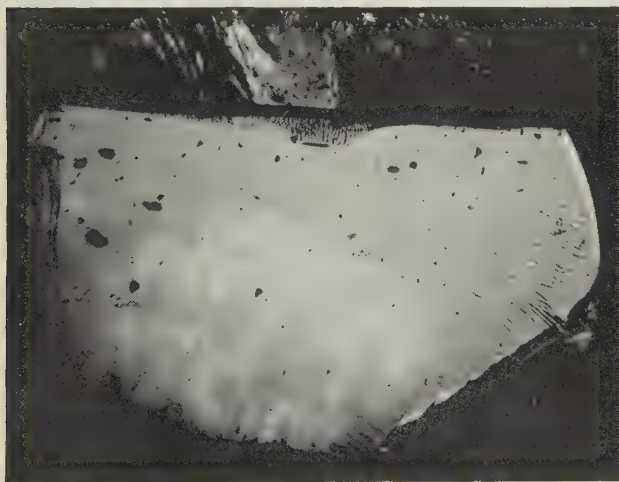


FIG. A.—Almost flat surface found in fractured calcite.

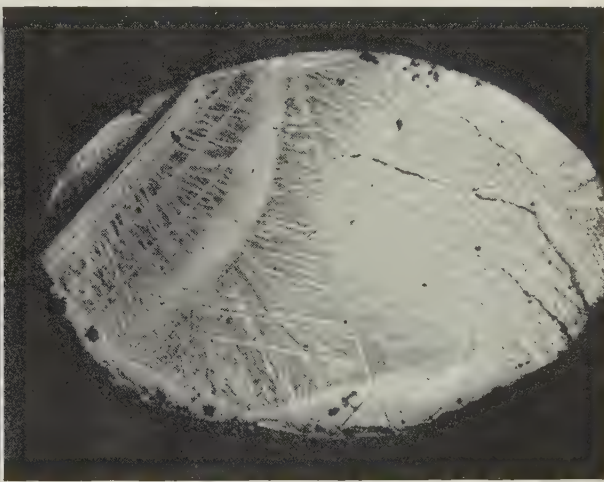


FIG. B.—River-line pattern, with steps arising over the whole of the fracture surface and converging in the direction of crack propagation.

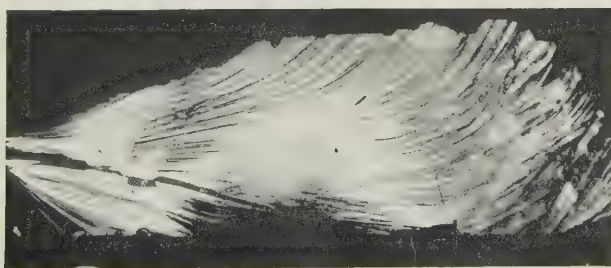


FIG. C.—System of steps radiating from the start of the fracture.

FIGS. A-C.—Types of Cleavage Fracture on Crystals. $\times 25$. (Pratt.)

(All reduced by $\frac{1}{8}$ in reproduction.)

Refractories for Low-Frequency Induction Furnaces *

Mr. J. C. HOWARD,† B.Met. (Member): The electric furnaces used by the authors of the two papers are very similar. They are both normal-frequency induction furnaces with a closed secondary loop in which the energy for melting is generated. In the case of the twin-chamber furnace operating on aluminium, the secondary loops are in a more or less horizontal plane and the two chambers are connected. This furnace is a 3-phase unit and, therefore, there are a number of channels—4 in fact, making a total of 3 loops. One of the purposes of the 2-chamber furnace is to be able to charge the material in the back chamber and to draw off the molten metal from the other and so, it is claimed, reduce the risk of carry-over of non-metallic impurities. Another claim for this type of furnace is that the flow of metal in and out of the loops is in a horizontal plane and, as compared with a furnace with vertical loops underneath the melting chamber, this reduces the fountain effect in the chamber and so reduces oxidation. In both cases, as already mentioned, the energy for melting is generated in the loop and circulating currents transfer the metal rapidly in and out of the loops. The metal temperature in the loop is naturally highest. It varies during the different stages of the melt and for the different alloys melted, but Dr. Cook and his co-workers have indicated that it can be as high as 200° C.

In the case of the aluminium-melting furnace, refractoriness, in the generally accepted sense, is not particularly important. The metal temperature even in the loops is not high relative to the fusion point of most refractories, and the oxides of the metals melted do not flux away the refractory walls. In fact, the reverse is rather the effect—the slot walls tend to build up with alumina, &c., and Mr. Thackwell refers to the regular slot cleaning that is necessary. The refractory must be sufficiently strong on its working face to withstand this cleaning operation, and in all cases of induction furnaces the refractory must be strong enough to resist the erosive effect as the metal washes in and out of the loop.

I wonder whether it will be agreed that the general conditions that obtain in the aluminium-melting furnace are severe, especially when these conditions are compared with melting furnaces generally. It would be wrong, though, to minimize the problem of providing a reliable lining for this type of furnace, as I well know to my cost. Aluminium seems to have the ability to seep through most refractories. Mr. Thackwell describes several methods and types of linings he has used. It appears that thickness and compactness of the refractory mass to prevent this seepage is a very important function. The densest lining has given the best results. I suggest the discussion may elaborate on this and provide comment on the grading and other factors which affect the denseness of the mass, for instance the water content. Considerable interest attaches to the mineral make up of the materials that provide this greatest density. Mr. Thackwell quotes 72% silica clay and 28% quartz, and for some purposes an addition of a further 10% quartz. Personally, I think greater detail in this particular aspect is well worth discussion. May I ask what is meant by "silica clay", because one wonders if the percentage of actual clay is not perhaps the most important single factor—not too much to cause drying cracks, but just enough to give the necessary green strength. This green strength is, of course, helped by the sodium silicate, but it is surprising that as much as 4% is used.

It will be seen from the paper by Dr. Cook *et al.* that many of the problems are considered to be similar to those of Mr.

Thackwell. When melting yellow brass, the conditions as regards refractoriness are similar to those encountered when melting aluminium. The oxides found are not corrosive, and the lining failure is quite often due to blockage of the channels. For other copper alloys, such as copper-nickel alloys and nickel silvers, and for copper itself, the refractory requirements are more stringent. Sometimes corrosive oxides are formed and, bearing in mind that the temperature of the metal in the slot is appreciably higher than in the bath, actual refractoriness of the slot walls is important if they are not to become enlarged. Dr. Cook's paper gives very interesting tables showing the causes of lining failure and how this incidence of slot wear is important with the higher-melting-point copper alloys.

I would draw your attention to the compositions of the lining material and also the grading of the grist. In my view this grading is perhaps the most important single factor. Many good refractories are spoiled by wrong grading, a point that I think is worthy of considerable discussion.

As I have said, there are many points in common in the two papers, as one would expect. The refractories used are similar, and so are the method of mixing with water, and the percentage of the water used. The similarity is illustrated by the fact that both advise that the conical pile should be avoided as tending to promote segregation. The importance of dense ramming, that the layers should not be too thick, that every effort should be made to prevent stratification, is stressed in the two papers. Both emphasize the importance of slow and careful drying and that the lining should be at such a temperature—and well soaked at that temperature—that it is not given a thermal shock when primed with the molten charge.

The paper by Cook, Cowley, and Broadfield emphasizes that the furnace transformer section is really the heart of the whole job, and that that is the point on which the greatest care must be exercised. The total relining time, including the relining of the body, is important, and any saving of body-relining time is helpful. Mr. Thackwell makes brief reference to cast linings. Casting of the melting chamber around a carefully rammed transformer block is successful, and it is suggested that discussion of how to line the melting chamber in the quickest manner, still having due regard to reliability, is worth elaboration. May I put in a plea for cast linings and say that for aluminium they work satisfactorily. Newer bonds for cast monoliths are now available and have a higher refractoriness than the *ciment fondu* that is largely used, so that cast melting chambers, even for copper, should be possible.

Mr. E. W. CASEWELL,‡ A.C.T., A.I.M. (Member): Collectively, Dr. Cook, Mr. Cowley, and Mr. Broadfield must have the largest fund of experience available of the Ajax-Wyatt low-frequency furnace, both with regard to the tonnages involved and also the range of alloys melted. Their paper contains a useful and concise account of the history, advantages, and theory of the low-frequency furnace, together with an appraisal of the refractory problems encountered.

On p. 296 mention is made of the effect of size and shape of the secondary channel, but the value of the paper would have been enhanced by the presentation of these dimensions in relation to the various alloys being melted. We prefer to use a $2\frac{1}{2} \times 1$ in. cross-section rather than the more usual $3\frac{1}{2} \times \frac{3}{4}$ in. secondary channel for the 600-lb. furnace. This shape presents a narrower front to the main electromagnetic

* Joint discussion on the papers by E. J. Thackwell (*Journal*, this vol., p. 283) and by Maurice Cook, C. L. M. Cowley, and E. R. Broadfield (p. 295).

† Director, Electric Furnace Co., Ltd., Weybridge, Surrey.
‡ Chief Metallurgist, Earle, Bourne, and Co., Ltd., Birmingham.

forces, it must be admitted, but the increase in thickness appears to provide an insurance against the formation of local constrictions. However, this particular problem cannot be considered without reference to the strength of the electromagnetic field as controlled by the number of turns on the primary coil and the primary voltage. While these points are perhaps just outside the discussion of refractories, it must be remembered that they are of the utmost importance to the ultimate successful working of a lining.

Major improvements have been made since Gillett and Mack quoted the figures given by the authors on p. 296, using fire clay/asbestos mixture, and today the aluminosilicate refractories seem fairly well established for the satisfactory melting of copper-zinc alloys. Norton in his book "Refractories" suggests that when temperatures above those normal for brass in the Ajax-Wyatt furnace are involved, the use of either fused magnesite, fused alumina, or magnesite/alumina mixtures should be tried.

We ourselves have retained the use of the usual aluminosilicate material for brass, the details of this material being virtually as shown by the authors in their Table II (p. 299). We should, however, prefer to employ fused alumina compositions when melting copper. Table A shows the significant details of this material.

TABLE A.—Approximate Chemical Composition and Grading of Fused-Alumina Refractory.

Composition, %		Grading	
		Mesh	%
Al ₂ O ₃	81.3	+ 8	31.0
SiO ₂	8.3	+ 16	19.5
Fe ₂ O ₃	1.0	+ 22	3.4
TiO ₂	2.4	+ 44	4.3
CaO	2.2	+ 60	2.0
Loss on ignition	2.6	+100	3.2
		+150	5.7
		—150	30.8

Sections III, 2 and 3, of the paper appear to deal adequately with the best technique for mixing, ramming, and pre-firing. As regards the depth of material rammed in each layer, it is useful to record that approximately 2½ in. of loose refractory—conveniently gauged by an average man's index finger—compacts to the 1¼–1½ in. mentioned as the desirable layer thickness. Probably the worst portion of the slot block to consolidate is around the base of the former. To this end we find it expedient to ram as far as one layer above the underside of the former and to cut and fit carefully the former into a groove in this layer. Similarly, the refractory is consolidated between the legs of the former right up to the bottom level of the Sindanyo side-boards, and then cut back to the contour of the bottom casing to receive the earth-shield assembly. This is shown more clearly in Fig. A where X and Y are the ramming levels referred to, and the cross-hatched portions represent the refractory to be removed.

While the need for uniform ramming of each layer is mentioned, no method of control is suggested. It is useful systematically to prod the surface of the layer with a pointed bronze rod. Any local soft spots are indicated by this method, and may be lightly re-rammed. If this is resorted to, care must be taken to avoid over-ramming which results in the spalling or lifting of the material beneath the hammer tools.

Coming to Section IV, dealing with lining life, our experience compares favourably with that of the authors. Using 600-lb. furnaces, the total average life when melting brasses is 1064 tons, with a maximum of 6243 tons. These performances are improved upon when using a 1200-lb. furnace, where the average life becomes 2071 tons with a maximum of over 13,000 tons for a lining still in use on brasses.

Mention has been made of the effects of the percentage of zinc, but the effects on the lining of addition elements to brass should also be considered. Lead tends to produce slot blockage by the formation of silicates of relatively low

fusion temperatures. Aluminium may well produce a general restriction of the channel-size, if brasses containing this element are melted continuously. On the other hand, tin appears to have little influence. Some elements have an opposite, scouring, action, and among these are iron and manganese.

A fortuitous set of conditions is therefore available which afford the means of controlling the cross-sectional area of

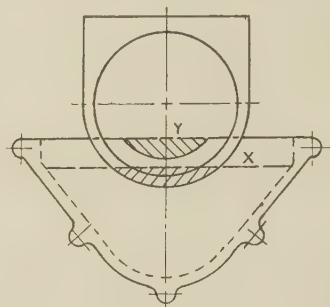


FIG. A.—Secondary-Channel and Bottom-Casing Assembly.

the channel. Judicious alternation of alloys seems to preserve the balance and the life of a 1200-lb. furnace working very roughly alternate periods of 14 days on leaded 58% copper and 70:30 brass, has been prolonged much beyond the 2000–3000 tons quoted by the authors on p. 305. This furnace is still in operation at over 13,000 tons.

One change of mixtures that does not appear to be recommended is to follow phosphorus-deoxidized copper with copper-zinc alloys, or vice versa. The effect is frequently to cause a fairly rapid enlargement of the secondary channel. This could be a result of the reaction between zincates and phosphates, produced on the hot face of the refractory.

In melting deoxidized copper in a 600-lb. furnace, aluminosilicate linings have given an average life of 343 tons, with a maximum life of 955 tons. The use of high-alumina refractories has increased these figures to 528 and 1514 tons, respectively. When melting phosphorus-deoxidized coppers there appears to be a continual change in the effective cross-sectional area of the secondary channel, as indicated by the recorded coil current. An unchecked decline results in very slow melting, whereas increasing current indicates erosion of the channel with the probable danger of a breakout of metal around the earth shield. It is important, therefore, to be able to control the size of the secondary channel during its life.

Occasional contamination of the bath may occur with such adventitious elements as zinc, iron, or lead. These are easily recognized on the relatively large surface of the bath, and since the quantity of the metal involved is fairly large, it is economic for their removal to be undertaken before pouring.

To enable the lining lives reported to be compared, Fig. B shows the incidence of lining failure in the same way as expressed by Cook, Cowley, and Broadfield in their Fig. 22 (p. 303). Fig. B relates to 600-lb. furnaces, which would normally presuppose a reduction of lining life. The main point brought out by both sets of diagrams is that having lavished care and attention on ramming, drying, and priming a lining, it can only be expected to melt up to 2000 tons of brass. The odd linings that produce the record figures must still be regarded as freaks because, as the diagrams show, some 70–80% of the linings fail before 2000 tons is reached.

It would appear therefore, that a really good lining is still very much a "lucky shot". In this respect the diagram shows that failures taking place below the average life amount to 60–65%. These are frequently due to very early penetration of zinc vapour through the pores of the refractory. Any treatment that could be given to the surfaces of the secondary channel which would seal these pores mechanically or initiate effective fritting of the surface, would pay immediate dividends.

The same observations are relevant for copper melting, but here the causes of premature failure are divided into slag blockage of the secondary channel when working with alumino-silicates, and miscellaneous operational causes with alumina linings. The normal failure for high-alumina

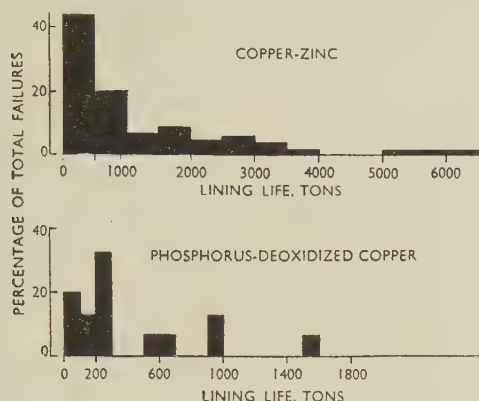


FIG. B.—Incidence of Failure in Ajax-Wyatt Low-Frequency Induction Furnaces.

linings is due to very slow erosion. Fig. C gives a schematic curve plotting the current at a constant voltage against the life of the furnace in weeks. The upper curve is for alumino-silicate linings, while the lower one is for a furnace built with high-alumina refractory. Soon after going into commission, both types of lining show a considerable drop in coil current, which is somewhat less for the alumino-silicate type of material. When the current is dropping in this type of lining, it is frequently due to the collection of debris

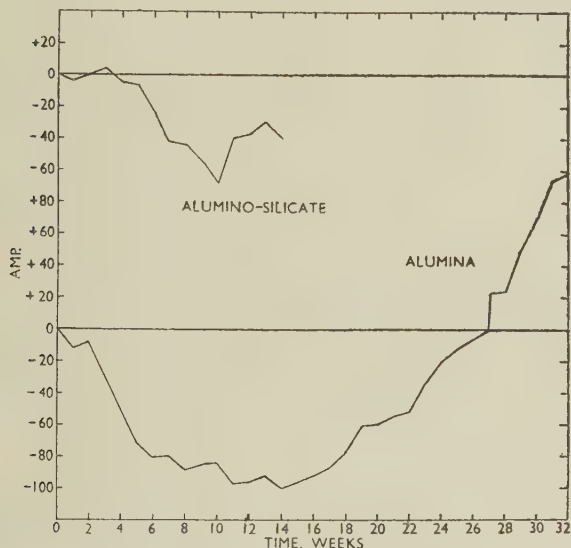


FIG. C.—Schematic Curve of Coil Current Against Life in Weeks When Melting Phosphorus-Deoxidized Copper.

at the base of the U, formed as the result of serious erosion in the upper limbs, so that eventually and quite unexpectedly a complete blockage frequently occurs. If observed immediately, this may, with luck, be removed by pushing an iron bar down the channel.

High-alumina linings suffer from an increased current reduction, but this would appear to be due to a formation of phosphate accretions on the refractory hot face. Here, resort to methods which would probably prove disastrous to an alumino-silicate lining may be made. As an alternative to

the rodding of the channels, the phosphate accretions may easily be dispersed by an oxidation treatment. It appears that the high-alumina lining is more chemically resistant both to copper oxides and phosphates, and consequently the effect of the slight porosity which might exist in a rammed lining is not nearly so fatal. With regard to the well-defined zones of altered refractory which occur around the secondary channel, it is interesting to note that there is considerable difference between the two types of lining material under discussion. The appearance of the alumino-silicate material is much more altered and is suggestive of a more easily initiated chemical attack, and this is frequently accompanied by a layer of marked porosity some $\frac{1}{2}$ in. back from the hot face. This porous zone appears to be absent in alumina linings, but they frequently exhibit instead a barrier layer rich in copper oxide.

Mr. R. W. RUDDLE,* M.A., F.I.M. (Member): I have read the paper by Dr. Cook, Mr. Cowley, and Mr. Broadfield with great interest, and I am quite sure that all those using Ajax-Wyatt furnaces for melting copper alloys will be very grateful to the authors for making their valuable experience so freely available. During the last few years the B.N.F.M.R.A., in co-operation with a number of its members including the authors' Company, has been conducting a study of the problems involved in melting the "difficult" alloys such as phosphorus-deoxidized copper and cupro-nickel in Ajax-Wyatt furnaces. As the result of both works trials and laboratory work (which are still continuing), the Association has gathered together a considerable body of information on the factors affecting the refractory lining of the slot, and it is satisfactory to note that our observations in the main agree well with those recorded in the present paper.

There are, however, as is only to be expected, a few points upon which we differ. On pp. 297 and 298, Dr. Cook and his co-authors describe the results of measurements of the temperature in the slot block, and from these data they extrapolate to derive figures for the temperature of the metal in the slot itself; these figures are summarized in Table I, from which it appears that the temperature in the slot is of the order of 100° C. greater than that of the metal in the furnace chamber. My colleagues at the B.N.F.M.R.A. have recently made actual measurements of the slot temperature in 600-lb. furnaces melting phosphorus-deoxidized copper and find that the temperatures are generally rather lower than indicated by the authors, being only 40° C. greater than the temperature of the metal in the furnace chamber. This figure was obtained with both normal and high melting rates.

A few years ago the tonnages of phosphorus-deoxidized copper melted per furnace lining were very small—50 tons/lining was then quite a good figure—and it is interesting to note how much greater than those reported in the past are the average figures of 441 and 262 tons/furnace lining quoted by the authors for, respectively, siliceous and alumino-silicate linings. No doubt the careful control of the moisture content of these refractories at 6%, combined with the use of material whose grading permits close packing and hence low porosity, has contributed to this very largely.

I am not sure whether the authors wish to imply that 6% of moisture is the ideal figure for all refractories, but I think they will agree that some materials, for example high-alumina refractories, should have a rather lower moisture content. That question of the correct grading of the refractory seems rather vexed, there being considerable divergence of view in the literature, and, like Mr. Howard, I feel it would be helpful if the authors could give us the benefit of their views on this point.

I was most interested to learn that the authors are actively pursuing the idea of using pre-fired refractory tubes as slot liners, as this was an idea we had some years ago. I should very much like to hear how these tubes have performed in the authors' trials.

On p. 301 Cook *et al.* discuss the drying and firing of newly

* Head, Melting and Casting Section, British Non-Ferrous Metals Research Association, London.

rammed slot blocks, but I wonder whether the temperature to which they fire the lining is really quite high enough in the case of the alumino-silicate refractory. The experience of some of the members of the B.N.F.M.R.A. with this refractory, and also with the high-alumina refractory, has been that, to ensure a really long lining life of the order of 1000 tons, the slot must be fired to at least 1300° C.

The discussion on pp. 304 and 305 of the paper of the reactions that take place between the metal and the refractory is most stimulating, and it is quite clear that the authors have made a number of very careful examinations of slot blocks which have failed in service. The reactions that take place in the slot are, as they say, extremely complex, and it is inadvisable to be at all dogmatic on this subject. Personally, I feel inclined to agree with many of the authors' views, although I wonder whether the destruction of the slot block is always preceded by penetration of metal into the refractory, followed by the oxidation of this metal and finally by reaction of the metal oxide thus formed with the refractory. May not, in some cases, the metal oxide be formed at the metal/refractory interface and subsequently penetrate into the refractory? I do not think that the observance of particles of metal at locations remote from the metal/refractory interface necessarily means that metal has penetrated to that location. It is possible that such droplets are precipitated from slag during cooling. It would be interesting if the authors could give us their views on the source of the oxygen with which the metal combines to form a slag. What proportion of this oxygen do they consider is derived from the melt, and what proportion permeated through the refractory from outside to react at the metal interface?

Both in the paper and in the discussion attention has been entirely centred on the resistance of the basis material of the refractory to attack by metal oxides, and the material used to bond the refractory grains together has been ignored. I wonder whether it is entirely right to do so. We have seen some indications in our work that the bonding clay may be slagged very much more rapidly than the refractory grains themselves, and I feel that it might be helpful if more attention were given in the future to the resistance of the bond to attack.

Finally, I notice that the authors refer to the use of both U and V channels, and I should be most grateful if they could tell us whether they consider one of these slots is superior to the other. There is little or no useful information in the literature on this point, and in view of their great experience the authors' views would be particularly welcome.

Mr. R. A. SKINNER,* B.Sc., A.I.M. (Junior Member): In Table II (p. 299) of the paper by Cook, Cowley, and Broadfield are shown the sieve analyses for two refractories, both giving very good grading curves with relatively high proportions of coarse and fine particles, and only small amounts of intermediates. I would like to ask whether these are the gradings of the refractories as supplied, or whether the material is regraded to get this sieve analysis?

The authors mention the use of different-sized hammers to help to obtain even ramming. We agree with this, particularly as some areas are very difficult to get at and are thus liable to under-ramming; in many cases, these are the most vital points, e.g. the narrow space between the slot and the earth shield, and under the point of the former. In this respect, we have tried the use of a T-shaped head which is found useful in reaching otherwise shielded areas.

The figures quoted in the paper show clearly that the larger furnaces have considerably longer lives. The authors point out that the minimum thickness of refractory between the slot and the earth shield is 2½ in. for a 600-lb. unit, as against 2½ in. for the 1-ton unit. Do they consider that this extra thickness is the reason for the improved life of the 1-ton unit or is it due to extra refractory thickness elsewhere, e.g. in the base of the furnace crucible? Many small producers

must find the 600-lb. unit more suited to their requirements, and it would be of great interest if the authors would give their views on the reason for the shorter lives of the smaller melting unit. Also in connection with this point of furnace size is any significant difference found for the smaller ½-ton furnace as against the 1-ton unit, in the relative proportion of lining failures due to each of the causes listed in Table IV (p. 302)?

The authors mention the important effect of operational procedure on lining lives, a point with which we would all agree. However, I would like to ask whether they are using dry covers for their melting, or fluid fluxes, and whether they think this might have any bearing on the life of units melting the low brasses, where slot blockage is the major cause of failure. I have recently heard that even such metals as aluminium bronze, which one would expect to be particularly liable to block the slot, can be successfully melted in an Ajax-Wyatt furnace if a substantial layer of a fluid flux is kept on the surface of the bath to absorb oxides as they form, thus avoiding their build-up into a blockage. It would be interesting to have the authors' views on whether a fluid melting flux might have similar effects in reducing slot blockage by such alloys as the leaded brasses.

The paper discusses the melting of the refractory alloys such as cupro-nickel and nickel silvers, where lining failure is very rapid and almost entirely due to slot enlargement. In other types of melting unit where severe refractory wear occurs, a solution has been found in water-cooling the back face of the refractory, e.g. in the high-frequency furnace and the water-cooled cupola. I wonder whether it might not be possible to apply something of this nature to limit the severity of attack in an Ajax-Wyatt furnace melting cupro-nickel.

The authors show us that one of the factors limiting the depth of refractory attack is the freezing of the metal and slag as it penetrates into the refractory. If water-cooling could be applied to give a steeper temperature gradient outwards from the slot surface, then lining corrosion might be limited to a relatively thin surface skin and the rate of wear appreciably lessened. It would seem to be relatively simple to cool the earth shield with a water-cooling coil, and the problem would then probably be how to cool the rear faces. This cooling would, of course, entail some loss of thermal efficiency, but with an average life of only 100 tons, or perhaps 7-8 days' working, it would seem that there must be a fair margin for a lowered thermal efficiency if the life could be increased. Could Dr. Cook and his co-authors say whether anything on these lines has ever been tried or whether there is some fundamental reason for its impracticability?

It has been asked earlier why a basic refractory should not be used for melting cupro-nickel, since the slags produced are primarily basic oxides. We have in fact tried a material based on fused alumina, but despite very careful ramming and firing, we experienced an exceedingly rapid slot enlargement, possibly due either to attack of the refractory bond or to the formation of low-melting-point mixtures of iron and manganese oxides with alumina.

Mr. G. J. BRITTINGHAM,† M.Met.E. (Member): The melting of copper in low-frequency induction furnaces has received much attention in Australia over a ten-year period; this method of melting is now utilized for the casting of upward of 12,000 tons of phosphorus-deoxidized copper annually. Indeed the bulk of the phosphorus-deoxidized copper used by the fabricating industry locally is drawn from castings, the metal for which has been melted in such furnaces.

In the early period of development work, "fused" magnesite linings were used, but although encouraging results were obtained, they were not such as to warrant perseverance. However, the technique of channel design and preparation which has now been developed may have permitted economic application of these basic linings, although at this stage no results in this connection are available. Attention has

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been focused in recent years mainly on the use of an aluminosilicate type of refractory, a commercial grade of which has been used with conspicuous success.

Furnaces of 300 kVA. rating, operated so that the amount withdrawn per casting cycle was approximately 1000 lb., but with a total furnace holding capacity of 2500 lb., have been used with complete success for tonnages in excess of 2000 tons/lining; the length of service life was up to ten months. In most instances where good tonnage figures were obtained from linings, the cause of the life ending was not lining failure but rather the fact that the continued use of the furnace lining became uneconomic owing to slower operation, on account of the tendency of the channel to become reduced in cross-sectional area—thus limiting the power input.

The conditions of operation were virtually continuous, i.e. the furnace was operated on full load except when the "stand-by" setting was used, as for instance during casting, or perhaps when some necessary furnace maintenance work required the suspension of melting.

The very favourable tonnage figures are undoubtedly connected with great care in preparation of the refractory and its subsequent ramming into position, but no small contribution is made by the channel (or loop) design, which has been modified largely on the basis of an analysis of the cause of channel failures experienced in the past.

Whilst a channel of rectangular cross-section has achieved great popularity in Australia for brass melting, its use on copper quickly revealed that it was impossible to obtain good tonnages; the main difficulties were associated with the corners of the rectangle, cracking frequently proving most troublesome. A loop of circular cross-section was obviously the strongest possible shape on mechanical grounds, and as most of the difficulties experienced had been traced to mechanical weakness of the loop in service, it was decided to adopt such a design. At the same time the loop was so constructed that any angles were eliminated, and it therefore became a combination of circular arcs and straight tangential sections, always utilizing a circular cross-section.

Since the life of such a channel is terminated in the majority of cases by closure during operation, it is evident that the larger the cross-sectional area of the channel can be made, the better the life that can be expected. This suggests that furnaces of higher power ratings can be expected to result in longer lining life, and certainly this deduction is confirmed by the results obtained from the 300-kVA. furnaces now in operation as compared with the 150 kVA. furnaces from which they were developed.

Channel design is important in respect to the electrical properties of the furnaces, and some progress has been made in regard to raising the power factor by alterations designed to reduce flux leakage and to improve coupling, but it is thought that the ultimate possible development has not by any means been achieved in these directions.

Mr. A. McMURDO *: As a representative of the refractories industry, I am especially pleased to see the care that has apparently been taken in ramming, drying, and pre-firing of the materials concerned. It has long been the opinion of the Company with which I am associated that such care is absolutely essential if an economic lining life is to be obtained. On the question of pre-firing, however, I should like to put forward some suggestions for the authors' consideration.

It is generally recognized in the use of refractories that the ideal course—though one not always economically possible—is to use a grade of refractory which, in the course of its manufacture, has been fired to a temperature greater than that at which it is intended to be used. The same principle will, of course, apply to the refractories used in low-frequency furnaces, especially in the region of the channel where, if high-temperature pre-firing can be employed in order to create a suitable ceramic bond in at least the surface regions, there will be less risk of shrinkage, with consequent cracking

in use, and also greater resistance to abrasion. May I suggest that something more could be done as regards pre-firing?

I appreciate that in the case of the higher-melting-point alloys higher pre-firing may be difficult, but surely one can obtain a temperature greater than 1100° C. One method might be to use Kanthal rather than Nichrome resistance elements.

The use of pre-fired refractory tubes in the channel region is of especial interest. I should certainly like to see this developed and extended, as it appears to me that by using such tubes it may be possible to employ refractories of the type desired in terms both of chemical composition and erosion-resistance. Further, if it is found possible to use refractories such as graphite, plumbago, or silicon carbide, which have relatively high electrical conductivities, the tubes themselves may assist in the re-starting of the furnace after freezing, and where a break in the channel circuit has occurred. These tubes may also allow the use of a castable material as a backing, as the density and porosity of the lining material need not be so critical as with the conventional rammed construction.

There are undoubtedly many problems associated with the installation and use of pre-fired tubes, and, indeed, in the case of certain materials it is not an easy job to make U or V tubes to close dimensional tolerances, but I feel that these difficulties could be overcome and that the subsequent improved life would be well worth the effort.

In the aluminium melting furnace mentioned, which is, I believe, of the Siemens-Schuckert type, the manufacture of the necessary channel tubes would, of course, not be very difficult, and I would suggest consideration of such a construction by the authors.

Finally, on the subject of the reaction between melt and refractory, Dr. Cook, Mr. Cowley, and Mr. Broadfield state that in the melting of copper-nickel alloys the manganese dioxide present reacts with the silica to form a fluid reaction product. If this is so, why use a siliceous material when it is possible to obtain a more or less silica-free material? Can the authors advise us whether a similar reaction occurs with alumina and basic materials and whether such materials have been tried?

Mr. J. C. HOWARD: It seems from the discussion on these papers that the density of ramming is a very important factor. Various methods have been described which different users have carried out. I am in complete agreement that density is the most important single factor and not only in the higher-melting alloys. When melting zinc in a Wyatt type of furnace, a uniform dense and compact mass is essential and we have found the best method of producing this is what we call "chicken-feed" ramming. In this method, one operator wields the pneumatic ramming tool, while a second sprinkles the refractory behind the ramming head, so that ramming and feeding-in of material are carried on progressively. This gives the most compact mass without any suggestion of layering. It is not too well favoured by the operators because it is more arduous, since there is not the minor rest period that occurs with the layer method at each stage of ramming. We prefer to adopt this "chicken-feed" method where there is any serious difficulty with any particular metal or alloy, but really it would be preferable in all cases if the operators could be persuaded to undertake it.

Considerable mention has been made of the oxidation of the metal and how this may affect the furring up of the slots. It is well known that the pinch effect results in the constriction of the metal in the slot, making it smaller in cross-section. It is reasonable to assume that this tends to set up a negative pressure relative to atmosphere in the metal in the slot, so that air is sucked in through the refractory and is in intimate contact with the slot. The oxidation products thus formed are deposited on the slot walls.

In practice, we have obtained some evidence to support

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this view. Particularly in melting aluminium we have noticed that if one slot tends to choke up very quickly, nothing can be done to improve it and we have found that the denser and more compact the rammed mass is made, the less is the tendency to fur. There are some indications that painting the outside of the slot block with sealing compounds to prevent this ingress of air gives improvement. Work has also been done with some success on maintaining an inert atmosphere around the transformer block. In fact, a patent has been taken out to cover this. The evidence so far available indicates that some metal oxidation is caused by air coming through the refractory mass, but it is not as yet conclusive.

Mr. THACKWELL (*in reply*): The contributors' comments, which cover experiences over a very wide field, are most welcome, not only for their technical interest but also in emphasizing the combined responsibilities of those engaged in various branches of metallurgy and engineering, in refractory chemistry, and in production planning, when considering at the basic design stage these particular types of melting furnaces.

In response to Mr. Howard's comments concerning the composition of the refractory materials, some clarification seems justified. The "silica clay" should perhaps be referred to as "clay", having a composition of approximately SiO_2 50, Al_2O_3 31%, the remaining 19% comprising Fe_2O_3 , BaO , MgO , TiO_2 , K_2O , &c. The additional 10% quartz and the use of 4% sodium silicate, was intended, as Mr. Howard suggests, to increase the green strength, in connection with mixes used for early linings formed by the flat-ramming method. All linings made by stitch-ramming, which proved the most successful technique, were formed with refractory that did not contain the additional 10% quartz nor the sodium silicate.

Regarding the general conditions obtaining in induction-melting furnaces, it was not intended to imply that these are severe compared with melting furnaces generally. The object in setting out the production and maintenance conditions affecting lining life was to stress the critical aspects warranting consideration when designing and forming a lining.

Consistent with durability, cast linings would seem to offer a very desirable time-saving during installation. It does not follow, however, that castable refractories could be adopted in furnaces where the use of rammed linings was intended, without revision of the design of the lining formers to meet the essential difference in the technique of pouring and floating down the refractory, compared with that of ramming.

The "chicken-feed" method of ramming, referred to by Mr. Howard, undoubtedly facilitates the formation of a compact layer-free mass. One very important reason for our adopting the technique of spreading and gauging 1 in. loose layers of refractory, is that a true working level can at all times be maintained, and that the slight ($\frac{1}{4}$ – $\frac{3}{8}$ -in.-thick) excess material allowed for cutting back when bedding the formers can be easily controlled and the time cycle thus adhered to. It is otherwise very easy to produce a horizontally off-level lining, giving rise to critical delays and drying of the refractory at a joint line whilst removing excess material (2 in. off-level over a bath floor 8 ft. \times 4 ft. can easily occur), before being able to begin bedding the formers.

Mr. Casewell mentions the practice of ramming one layer ($1\frac{1}{4}$ – $1\frac{1}{2}$ in. thick) above the underside of the slot former, and of cutting and fitting the former in a groove in this layer. Undoubtedly the cutting back of compacted refractory ensures sound material beneath the formers. However, as stated in the paper, we adopt the practice of ramming about $\frac{1}{4}$ in. high above the former-base levels, and then cut away the excess material over the surrounding area. Access is thus gained for side- and end-checking for full contact of the base of the slot formers in particular. The ramming of the side walls of the horizontal slots is also begun from the base line; otherwise displacement of pre-compacted refractory during the continuation of ramming seems likely to occur by taking up the side clearance created in the $1\frac{1}{4}$ – $1\frac{1}{2}$ -in. layer when fitting the slot former. Moreover, moisture loss or variation by intermediate damping during the interval involved in

fitting the slot formers occurs within the thin walls of the slots, where uniformity in all respects is most desirable.

Mr. Ruddle draws attention to the difference in temperature between metal in the slots and in the furnace chambers. He compares the figure of 40° C., arrived at by the B.N.F.M.R.A., with the temperature difference of the order of 100° C. derived from the paper by Dr. Cook and his co-authors; whilst Mr. Howard, quoting from the latter source, receives the impression that it can be as high as 200° C. The temperature variation occurs at the part of a lining having the least mechanical strength, and where metal leakage is usually fatal. The temperature differences are, of course, bound to vary according to the type of induction melter—i.e. horizontal- or vertical-slot design—the alloy melted, and the melt stages. However, there seems to be an opportunity here for the establishment of more precise information regarding temperature differences and resulting gradients, to the advantage of manufacturers and users alike in the future design of furnace linings and the development and application of durable refractories, whether rammed, cast, or pre-fired.

Mr. Skinner has commented on the critical part of a lining where design imposes limitations on the slot-wall thickness. It is doubtful whether a difference in thickness of $2\frac{1}{2}$ in. compared with $2\frac{3}{8}$ in. would materially affect lining life, at least when melting aluminium and discounting erosion. In this most vital area, experience indicates that the ability to form a uniformly very dense layer-free lining is the greatest deterrent to failure by cracking or contamination of the refractory. Associated with this is the control of moisture content of the mix so as to discourage crack formation during pre-firing. Again, the heat applied to these relatively thin walls when pre-fired, if not carefully balanced by judicious use of the transformer-coil-cooling fan to chill the earth-shield side, can result in the excessively rapid drying out of the walls, with the accompanying risk of crack formation.

Mr. Brittingham quite rightly upholds the merits of a slot having a circular cross-section as possessing the greatest mechanical strength. Such formers, although readily applied vertically, present difficulty during ramming if used horizontally, owing to restricted access along the base. Ramming and then cutting away to, say, half-depth to fit the former offers a solution to ramming problems, but as mentioned earlier, the hazards of displacement in depth of compacted refractory and loss of moisture at the intermediate layer must not be overlooked. The combination of circular-section pre-fired slot tubes surrounded by a cast refractory lining which would float more readily around the tube profile, offers an attractive alternative.

Mr. McMurdo refers to the raising of pre-firing temperatures of a lining to a level capable of creating a ceramic bond at least in the surface regions, especially in the melting slots. Whilst this is a very desirable objective, our experience has been that rammed linings pre-fired to temperatures of 950°–1000° C. have always developed contraction cracks, obviously incapable of closing again, when the lining attained the normal operating temperature for aluminium alloys of, say, 730° C. Minimizing of the moisture content in mixes alleviated but did not eliminate cracking. It is a feature admittedly liable to aggravation by the complexity of shape and balance of mass in the lining. To ensure sound linings, it ultimately proved best to restrict the maximum pre-firing temperature to a level consistent with the operating temperature of the furnace, allowing progressive curing of the lining in use. For this reason, refractories having a low fritting temperature are desirable in induction-melting furnaces for aluminium.

Dr. COOK, Mr. COWLEY, and Mr. BROADFIELD (*in reply*): We are grateful to the many contributors to the discussion for the interesting comments which they have made in the light of their own experience. Mr. Casewell and Mr. Skinner, particularly, have recorded some of their own findings and it is gratifying to note the measure of agreement in many directions. There are, however, a number of questions to be answered and various points which call for further comment and explanation.

Mr. Howard emphasizes the importance of correct grading,

while both Mr. Ruddle and Mr. Skinner comment on our data and ask for further views on optimum particle-size distribution and moisture content. There is, of course, a theoretical particle-size distribution for maximum packing density, but, in fact, considerable divergence from this theoretical ideal is possible with little, if any, detriment to the rammed density. While normally refractories are supplied suitably graded, a certain amount of checking and control is necessary to ensure that standards are maintained. Water in normal amounts acts as a lubricant and increases the density obtained by ramming, but excessive amounts allow flow to take place under the hammer. The optimum water content probably depends more on the physical make-up of the mix than on its chemical composition. It is therefore possible that the particular high-alumina refractory used by Mr. Ruddle required a somewhat smaller water addition.

There is, we are afraid, no short answer to Mr. Ruddle's question on channel design. It is, of course, true that the U-shaped channel has a longer length of metal in close coupling with the primary circuit than the V channel, and the former should, therefore, have slightly better efficiency. However, many factors in design influence the electrical characteristics, and this single factor is not necessarily the most important. With charges such as brass, in which blocking of the channel is experienced, the V-shaped channel has advantages in its ease of cleaning. Furthermore, the V-shaped channel does, in fact, result in more uniform electromagnetic as well as thermal circulation of the metal. Mr. Casewell has indicated some of the factors which influence the choice of channel section, and we agree broadly with his analysis. Channel shape is a compromise between that giving the maximum coupling effect, which will be rectangular with as large as possible a dimension parallel to the electromagnetic field, and a round section, which is the least susceptible to blockage. In any event, where erosion occurs the channel tends to become rounded in use.

In answer to Mr. Skinner's question, we confirm that extra thickness of refractory is one of the main reasons for the improved service life of 1-ton units as compared with the small 600-lb. furnaces. The vulnerable regions are between channel and earth shield and between hearth and earth shield, and small furnaces suffer a high proportion of failures involving metal penetration. Adequate cooling of earth shields is important for this reason, and recently we have increased the forced-air draught over the primary coils on 600-lb. furnaces with beneficial results. In this connection, Mr. Skinner's suggestion for water-cooling should be advantageous if safe designs can be evolved. Points made by Mr. Brittingham on the influence of size on service life are, in our opinion, sound. In the larger furnaces the greater channel cross-section permits easier cleaning, and changes in cross-sectional area for a given life are proportionately smaller. We would confirm that furnaces are often withdrawn from service prematurely because continued use is uneconomic owing to slowing down of the melting rate. Either increased or decreased channel cross-section can lead to this result.

Temperature in the furnace slot has come in for some discussion, and Mr. Ruddle reports a temperature difference of only 40° C. between slot and furnace body in a 600-lb. furnace melting deoxidized copper, although he does not state the position in the slot at which the temperature was measured, or whether he found an appreciable temperature gradient between the apex and mouth of the slot. It is evident that slot temperature will depend on the alloy melted and the maximum bath temperature employed, and that it will vary during the melting cycle, while again the condition of the loop is bound to have a considerable effect. In the circumstances we feel that more precise figures than the temperature ranges quoted in Table I (p. 298) are unjustified. These, it should be noted, are approximate maximum temperatures attained in the channel, and not metal temperatures taken at some given stage in melting.

Several contributors refer to high-alumina refractories, and we are interested to note the good results obtained by Mr. Casewell with these materials. We would agree with Mr. McMurdo that, other things being equal, greater resistance

would be expected to the more aggressive metals such as cupro-nickel by alumina and other basic materials than by the siliceous linings which we presently favour. The advantage from siliceous materials is derived, we believe, from the small expansion of quartzite on firing, which compensates for the natural firing shrinkage. Thus in siliceous linings the main mechanism of failure is slagging, while in our experience high-alumina materials fail by cracking or spalling, a tendency aggravated by the natural firing shrinkage. Mr. Ruddle suggests that slagging may occur preferentially at the interstitial clay bonding between the more refractory grains. While this is possibly true with fused alumina or magnesia, where there is little interaction between basis and bond in firing, it is certainly not our experience with siliceous linings, and there is no question of preferential attack of the bond being primarily responsible for lining wear.

The possibility of using pre-fired channel-lining tubes has aroused wide interest. Trials of such tubes appear to have been undertaken in several places with only moderate success, although Mr. Howard points out that recent improvements have been brought about in pre-formed or cast monoliths. It is evident that if a satisfactory furnace structure can be made and fired, incorporating such a monolith, then it should have a long service life. The construction of the furnace partly from a pre-fired block and partly from a lining rammed *in situ*, involving as it does a sharp change in properties of the component materials, is no mean problem. On firing such a composite structure, dimensional changes occur in different senses in the two component parts and many possible sources of disruptive stresses present themselves. In our view a single integral rammed lining with its uniformly graded firing from surface to interior is more likely to provide a physical structure resistant to the thermal and mechanical stresses involved in furnace operation. For similar reasons we do not share Mr. Ruddle's and Mr. McMurdo's views about higher temperatures of pre-firing. Furthermore, many refractories display a marked increase in permeability with temperature increase, and this is another sound reason for restricting the temperature of firing to the maximum molten temperature likely to be encountered in service.

It seems to be well established that oxygen from the air diffuses through the refractory wall, particularly in the channel, to form metal oxides which may either deposit in the channel as a solid oxide accretion or react to form low-melting slags. Mr. Howard suggests that the negative pressure set up by the pinch effect might suck air through the refractory. However, there is no doubt that diffusion can occur without postulating such negative pressure. Any design of furnace or method of sealing which would prevent the ingress of air through the refractory walls would be of considerable value, and would be expected to lead to an increase in furnace life, but it should be pointed out that this involves more than just the sealing of the outer casing of the channel. How far oxygen is carried down from the exposed metal surface will depend a great deal on operational practice, and the preservation of a thick charcoal layer can reduce this source of oxygen to a minimum.

We accept Mr. Ruddle's finding that metal droplets are, in certain instances, precipitated from slag during cooling. However, molten metal itself undoubtedly permeates under hydrostatic pressure into the cracks and pores in the lining of the secondary channel, and appears to be halted only by oxide deposition at distances which may extend as much as 2 in. from the metal/refractory interface. When such metal particles are separated by crushing and flotation, they can be shown to have compositions approximating closely to that of the main charge.

Finally, Mr. Skinner suggests the use of a fluid flux layer, particularly on aluminium bronze and leaded brass, to absorb surface oxides and to prevent their transfer to the slot. In practice the furnace should not be tilted to an extent which allows surface dross to enter the slots, and in any event the hard oxide accretions which form in the slot are not derived in this way. The use of fluid fluxes, moreover, gives rise to a variety of operating difficulties, and our own preference is for a dry cover.

Discussion

The Working Properties of Metals *

Dr. J. C. CHASTON,† B.Sc., A.R.S.M., A.Inst.P., F.I.M. (Member): These papers are to be welcomed particularly as representing a metallurgical approach to the problem of working, as distinct from the more general engineering approach to the subject. For too long, perhaps, research on the rolling of metals has been dominated by considerations of power consumption. The engineering approach, of course, is undoubtedly of prime importance to the rolling-mill designer and perhaps also to the metallurgist concerned with obtaining high outputs of ductile materials, but it is often only incidental to the non-ferrous metallurgist who is dealing with less readily worked metals and alloys, which are often only too ready to crack.

The main problem in working many materials is, as is clearly indicated in the paper by Dr. Hundy and Dr. Singer, that in rolling as in wire-drawing, the deformation is never pure and seldom simple. The outside of the work tends to be stretched more than the inside, and the complex stresses produce a correspondingly complex pattern of straining.

While the general conclusions of this paper are of considerable importance, I think that too much emphasis should not be laid on the individual results. I doubt, for instance, whether it is true that reductions of more than 40% always produce uniform hardness throughout rolled sections. Moreover, even if the hardness is uniform throughout a section, this result cannot be accepted as definitely proving that the amount of deformation is uniform throughout. Further, in considering the paper, it is as well to remember that tensile prestrain is in itself inhomogeneous.

I am not entirely convinced, moreover, by the results of the work comparing the effects of one large pinch and many small ones. The authors conclude, from the observation that a reduction of 10% in one pass resulted in an inhomogeneity factor of 12, whereas a similar reduction in ten passes resulted in an inhomogeneity factor of 5, that one large pass causes more surface deformation than ten small ones. It would be interesting to observe the difference between one really large pass of 40% and several small passes, particularly since the authors find that the one large pass produces uniform hardness throughout the section.

Finally, in this paper, I think that the authors' references to die angle in wire-drawing are a little over-simplified. It would be useful to know the length of the parallel portion in their dies, as well as the approach angle, and to learn a little more about the shape of the dies used.

To turn now to the paper by Dr. Alder and Dr. Phillips, I have never been very happy about the use of compression tests for comparing the behaviour of metals in deformation. In any laboratory test it is inevitable that some friction must exist between the end-plates and the work, and though this may be small, it undoubtedly influences the mode of deformation. I am therefore surprised that the authors did not carry out a few tests, at least, using specimens of various shapes in an attempt to evaluate the effects of friction. I find the paper a little difficult to follow on account of the method of presentation. It would, I think, have been better to give the results of the effects of strain rate and temperature on the deformation of copper and steel in the form of curves rather than as somewhat elaborate tables.

The third paper, by Messrs. Leech, Gregory, and Eborall, on the hot tensile test, is most interesting as representing a determined effort to find a laboratory test of hot working. It does appear to me, however, that in devising this test the

authors have worked along entirely the wrong lines. In my view it is impossible that a tensile test which deliberately avoids complications due to inhomogeneous working can be a measure of the behaviour of a metal when it is deformed by such a complex procedure as hot rolling. The two conditions are just not comparable. The authors put forward as a justification of their viewpoint the result that in their tests percentage reduction of area observed in specimens submitted to their hot impact tensile test was just about equal to the percentage reduction which caused visible cracking in one pass in their rolling mill. This is surely the kind of correlation which has from time to time been observed between the rolling behaviour of a difficult alloy and the phases of the moon. It seems inconceivable that further experience will substantiate a general relation between such entirely unrelated quantities. I would suggest that if progress is to be made in developing a laboratory test, it will be necessary to devise some method of measuring the amount of inhomogeneous deformation that can be tolerated. If this could be done, an important step would have been taken towards establishing clearly the conditions responsible for celery cracking, transverse cracking, and other similar ills that now beset the metallurgist.

One method of achieving this result might be by the use of standardized laboratory rolling tests of progressive severity, using perhaps both sheet and grooved rolls and possibly including observations of the effect of driving one of the rolls faster than the other.

One final point may be mentioned with regard to the paper by Leech, Gregory, and Eborall. As it stands, Fig. 3 (p. 349) is very obscure. Could the significance of the various lines be marked more clearly?

Dr. D. E. R. HUGHES ‡ (Member): The test described by Messrs. Leech, Gregory, and Eborall has the advantages of simplicity and of using a standard piece of test equipment. Furthermore, it has been shown to yield results which are related to the behaviour of certain non-ferrous materials in commercial hot-working operations. However, the correlation with hot-working behaviour shown by the tests on cast brasses and bronzes refers to what might be termed "large-scale" effects, which are well known, and which would probably be revealed by almost any mechanical test carried out under appropriate conditions. For such purposes, any test which gave a measure of capacity for deformation would suffice, and the only consideration would be which test was the most convenient to carry out. This would apply particularly in the case of hot rolling or press-forging, and in cases where it was desired to ascertain how a new or modified alloy was likely to behave in relation to well-known ones.

It seems to me that any really satisfactory test for hot workability should give a clear-cut indication of the optimum working temperature, yet none of the results presented in the paper shows this. It may be, of course, that if the authors had given results of tests at higher temperatures, a maximum in elongation or reduction of area would have been noticed at some temperature below that of incipient fusion. Can the authors say, for instance, whether they carried out any tests on the cast brasses (Fig. 4, p. 349) at temperatures above 850° C.? The answer to this may well be that for the purpose they had in mind such tests were quite unnecessary, and that the indications given by the curves of Fig. 4 are sufficient to determine a satisfactory hot-working temperature.

It is unlikely, however, that indications of this type would

* Joint discussion on the following papers published in the *Journal*: J. F. Alder and V. A. Phillips, this vol., p. 80; E. A. Leech, P. Gregory, and R. Eborall, this vol., p. 347; B. B. Hundy and A. R. E. Singer, this vol., p. 401.

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be sufficient for all types of hot-working operation. In particular, the case of rotary piercing of billets for tube manufacture is one where a tensile test (admittedly not an impact tensile test, but one carried out at fairly fast rates of the order of 1.0 sec^{-1}) has been found not to give such good correlation with practical hot-working behaviour as does a torsion test. Fig. A shows the results of a torsion test on copper of wire-

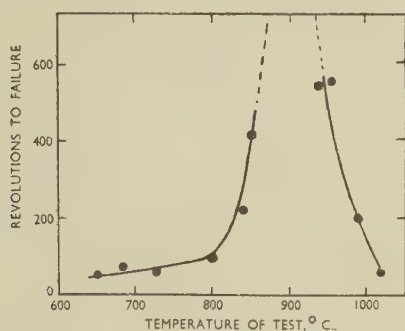


Fig. A.—Torsion Tests on Copper. Speed 100 r.p.m. (1.34 sec^{-1}).

bar-quality, in which the number of revolutions to failure is plotted against test temperature. There is a well-marked maximum in the region of 900°C ., which is the temperature used for the rotary piercing of this material. Tensile tests carried out on the same material showed no marked change in reduction of area or elongation until the sudden drop associated with incipient fusion at about 1060°C . Further illustration is provided by Fig. B, which refers to torsion and

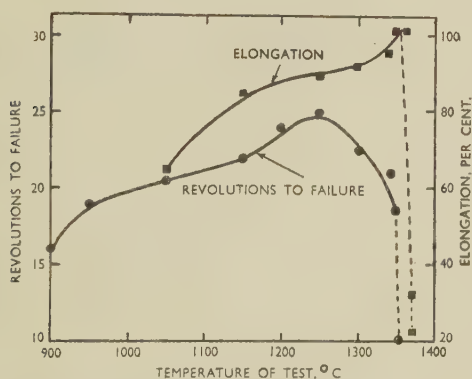


Fig. B.—Torsion and Tensile Test Results on Austenitic Stainless Steel (ESL). Torsion test: 100 r.p.m. (1.34 sec^{-1}). Tensile test: 0.2 sec^{-1} (initial).

tensile tests on a stainless steel; the number of revolutions to failure and elongation, respectively, are plotted against temperature. The torsion tests indicate a fairly well-marked maximum at 1250°C ., followed by a gradual fall up to about 1350°C ., above which temperature there is a sudden drop due to the onset of incipient fusion. The elongation in tension, however, increases slowly right up to the temperature of incipient fusion. The best temperature for the rotary-piercing operation for this material, however, is around 1250°C ., and this temperature is fairly critical in spite of the fact that the ductility of the material appears to be excellent over a wide temperature range—in fact the reduction of area in tension was generally close to 100%, so that a plot of this quantity would have been useless.

This indication of a maximum in revolutions to failure at a

temperature well below that of incipient fusion seems to be a characteristic feature of the torsion test—the feature which has been most useful as regards correlation with the rotary-piercing operation in tube-making. This has been the conclusion of other workers.

The reason for the maximum is not clear. One would expect any test to show, in the absence of phase changes, a steadily increasing (or perhaps more or less constant) capacity for deformation as the temperature increases. In general, this seems to be the case if one uses a simple tension test, and takes elongation or reduction of area as a measure of capacity for deformation.

The mode of deformation during the rotary-piercing operation is complex, however, the billet being subjected to simultaneous ovaling of the cross-section and a longitudinal twist. The torsion test, as used by myself, suffered from the disadvantage (from the fundamental research point of view) of inducing a rather complex stress system in the test-piece, and it is difficult to see how this could have been avoided. It may be, however, that the form of the curve relating revolutions to failure with temperature is connected with this complex stress system, and that it is precisely because of this feature that the torsion test has given such good correlation with tube-making practice.

It was thought that the occurrence of the maxima in the curves at temperatures well below incipient fusion might be connected with a temperature rise due to the work done on the test-piece. An appreciable rise in temperature does occur, of course, but it was not considered that this was sufficient to account for the observed characteristics since:

(1) The effect of increasing the testing speed should be to shift the maximum to lower temperatures. Although this has been observed to happen in isolated cases—particularly for mild steel—it is by no means general.

(2) No evidence of incipient fusion has ever been found on micro-examination of broken torsion test-pieces, unless the testing temperature was very close to that of incipient fusion.

Finally, I should like to raise one point concerned with the size of test-piece used by the authors. The gauge-length is so short that it is probably true to say that there could never be any period of uniform extension under uniaxial tension. There would be “necking” from the start, so that all the deformation would take place under the influence of a triaxial stress system. This could be an advantage from the point of view of correlation with practice, because indications similar to those of the torsion test might be obtained. This is another reason for asking the authors about any tests they may have done at temperatures right up to the solidus.

Dr. J. V. LYONS,* B.Sc., A.I.M. (Member), and Mr. F. A. HODIERNE,* B.Sc., A.I.M. (Member): The paper by Messrs. Leech, Gregory, and Eborall has shown that a good correlation can be obtained between the results of the impact tensile test and the behaviour of certain copper-base alloys in a practical hot-working operation. In a similar manner, we have been using for some years the hot torsion test described by Dr. Hughes† to assess the hot-working behaviour of metals in tube-making operations. The usefulness of any such laboratory tests is often challenged on the grounds that only tests which closely simulate the conditions obtained in practice can possibly give the correlation required. Whilst the value of this type of simulative test is evident, such tests can often be very difficult, if not impossible, to devise, particularly where complex operations such as rotary piercing or tube extrusion are considered. In such cases, tests which attempt to measure some fundamental property of the metal constitute the only possible approach.

We are therefore in sympathy with the general outlook which prompted the work on the impact tensile test, but there are a few points of detail on which we are not in full agreement with the authors. In particular, the possible effect of strain rate on the results obtained does not appear to have been given

* Tube Investments, Ltd., Department of Development and Research, Birmingham.

† D. E. R. Hughes, *J. Iron Steel Inst.*, 1952, **170**, 214, and preceding contribution.

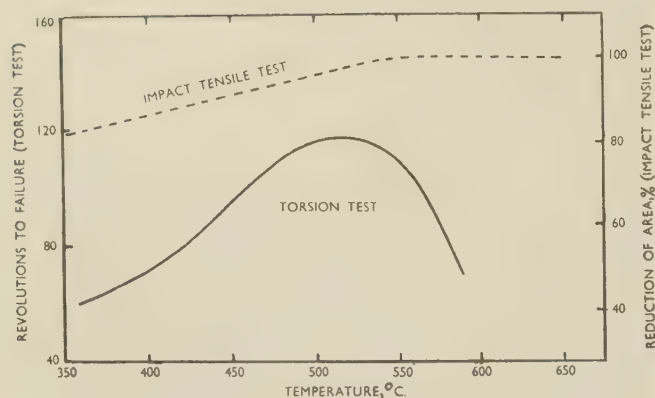


FIG. C.—Pure Aluminium.

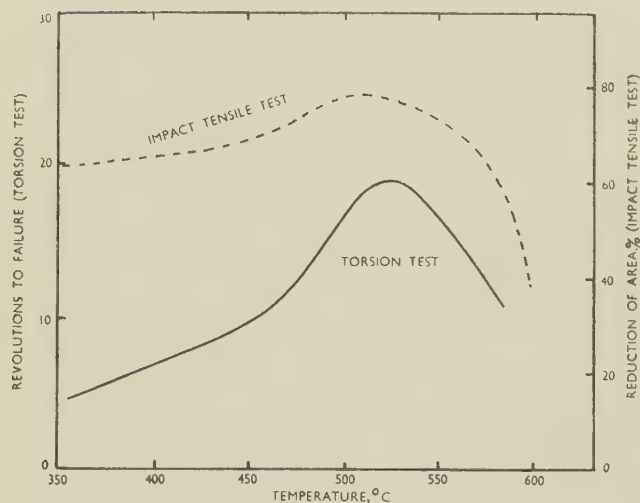


FIG. D.—Aluminium-2% Magnesium Alloy.

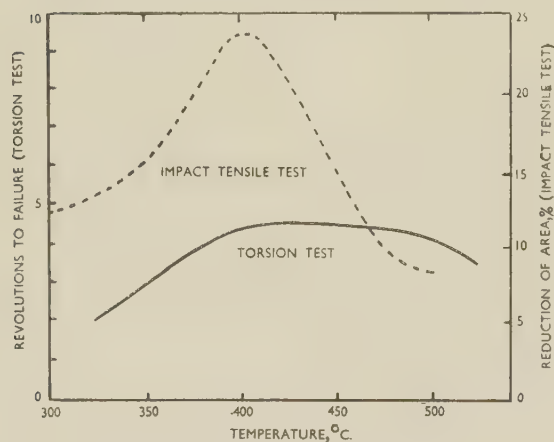


FIG. E.—Duralumin-Type Alloy.

FIGS. C-E.—Comparison of Results of Impact Tensile and Torsion Tests.

due consideration. The paper by Dr. Alder and Dr. Phillips indicates that strain rate can affect the resistance to deformation, and Dr. Hughes* has also shown, in the case of mild steel, that strain rate can alter the capacity for deformation and the

apparent optimum hot-working temperature. In the impact tensile test, the initial strain rate is stated by the authors to be considerably higher than the strain rate in actual hot-rolling operations; furthermore, the strain rate in any tensile test increases rapidly as necking of the specimen occurs. Thus the strain rate at fracture depends upon the degree of necking and hence varies with the workability of the material. In contrast to this, the dimensions of a torsion test-piece do not alter significantly during testing, so that the strain rate remains constant. The strain rate does, of course, vary from the axis to the outside of the specimen, but the value at the surface is known and can be altered. The strain rate can thus be made to approximate to practice, and its effect can readily be investigated.

We have had the opportunity of comparing the impact tensile test and the torsion test on a number of cast aluminium alloys. The impact tensile tests were carried out on the actual equipment described in the paper by Leech, Gregory and Eborall, and we make acknowledgement to the B.N.F.M.R.A. for their kind permission to use their apparatus.

There are certain interesting differences in the results produced by the two tests. In Fig. C there is shown the variation of reduction in area in the impact tensile test, and the revolutions to failure in the torsion test, over the same temperature range, for cast commercially pure aluminium. This illustrates one disadvantage of a tensile test when applied to a very ductile material; the curve approaches a figure of 100% reduction of area and remains near that figure, so that the results are then insensitive to variations in ductility, whereas the torsion tests are able to show a definite maximum.

In Fig. D the impact-tensile and torsion-test results are shown for a cast aluminium-2% magnesium alloy. Here the results of the two tests are similar, and the optimum working temperature indicated is in reasonable agreement with practice.

The results of the two tests when applied to a cast Duralumin-type alloy are shown in Fig. E. Here, the torsion test shows no pronounced maximum, but a comparatively uniform workability over a wide temperature range, whereas the impact tensile tests exhibit a maximum at 400° C. This latter result seems to be at variance with practice, since the workability of Duralumin is not normally found to decrease with increase in temperature over the range 400°-475° C. In this case, therefore, the results of the torsion test seem to be in somewhat closer agreement with practical experience.

We should like to conclude with a final suggestion that these differences in results may be due to differences in the strain rates used, and that an attempt should be made to obtain as close a correlation as possible between the strain rate in the tests, and that occurring in practice, unless it has been determined that the particular type of alloy under investigation is comparatively insensitive to strain-rate variations.

Professor H. O'NEILL,† M.Met., D.Sc., F.I.M. (Member of Council): The determination of the elongation value at hot-rolling temperatures by a reliable impact tensile test seems to be quite a reasonable method of assessing liability to edge-cracking during hot rolling. The evidence produced by Messrs. Leech, Gregory, and Eborall for the existence of a close relationship between these two quantities for copper-base alloys is therefore valuable, and justifies the extension of such work to other metals. It is by publication of these and further data that we can decide upon the merits of the test.

The use of indentation methods should not be overlooked, however, as they might prove to be simpler and less expensive. They also permit the introduction of the lubrication factor, which is not directly possible with the tensile test. Kenneford and I put before the Institute in 1934‡ some results obtained on the edge-cracking of white metals in the static Mallock cone test at room temperatures. Further work on the Mallock test has since been completed. Dynamic tests on this principle at elevated temperatures could easily be devised. It may be

* D. E. R. Hughes, *loc. cit.*

† University College, Swansea.

‡ A. S. Kenneford and H. O'Neill, *J. Inst. Metals*, 1934, **55**, 49.

recalled that Brinell's work with the ball indenter, published in 1901,* included some satisfactory determinations of the percentage elongation of steels. This procedure developed out of the routine "forging test" in use at the Fagersta steel-works and consisted of bulging the edge of a steel specimen with a 5-mm. ball until cracking began.

As regards the paper by Dr. Hundy and Dr. Singer, the study of inhomogeneity in cold-rolled metals by means of plastic indentation tests has been fruitful, but the latter test introduces complicating effects of its own superimposed upon the original specimens. Particularly is this the case as regards internal stress and the Bauschinger effect, and hardness explorations of the metal below large indentations show certain anomalies. One example can be observed in a paper by Pope and Mohamed† and another in some work from Swansea which includes evidence of local work-softening.‡ Exploration of strain distribution by electrode potential or some non-deforming process would be desirable.

Mr. J. G. WISTREICH,§ M.Sc., D.I.C., A.M.I.Mech.E. (Member): I should like to support Dr. Chaston's plea for more graphs. Could not the Institute, in cases like that of the paper by Dr. Alder and Dr. Phillips, deposit complete sets of data in the Library? This would satisfy those who want to make use of the full information and it would not claim any space in the *Journal*?

Materials are taxed not only by manufacturing processes but also by tests; the links between the two are founded on evidence, on theory, or on superficial similarity between test and process. The first is, of course, decisive. In the absence of comprehensive evidence correlating material performance in test and process, one has to reckon with personal preference in the matter of faith in theory or in the principle of analogy. I shall not say what my preference is in this matter, but it seems important that an analytical test should not be damned for not being simulative, or vice versa. Where new tests are being devised, one should decide beforehand which type it is going to be. The test suggested by Professor O'Neill seems to me to be a hybrid in this respect: it resembles the cold-heading test which is simulative, and it has something in common with Alder and Phillips' tests, which were analytical. Professor O'Neill has criticized the latter on account of the complexity of deformation in the presence of friction, but the cone test seems to me even more complicated, with or without lubrication.

I have read the paper by Dr. Hundy and Dr. Singer with much interest and admire their ability to learn so much by such simple means. The authors will agree with me that their work is exploratory rather than definitive, and my further remarks are addressed to those who may wish to delve more deeply into the phenomena uncovered by the authors. I regret their carping reference to the grid technique. Admittedly it is tedious, but it is more precise and certainly more to be trusted than hardness measurements. The term "inhomogeneity factor" is to be deprecated; it may not have deceived the authors who know about the Bauschinger effect and about the non-linear relation between hardness and deformation, but it might mislead others less well informed. I doubt whether fully work-hardened metals deform less homogeneously than annealed ones; plasticity theory suggests that the converse is true. I am attracted by their explanation of the secondary inhomogeneity, but as matters stand in the paper, it is inspired guesswork which calls for verification. I am not, however, inviting the authors to go through the tedium of slip-line-field calculations; they can find all the support they need in the paper by Siebel and Hühne.|| These authors, of course, measured deformation proper by the grid-line technique.

My criticisms do not in any way detract from the valuable observations made by Dr. Hundy and Dr. Singer, particularly of the effect of lubrication on surface hardness.

Mr. P. M. COOK¶: My remarks will be confined to the paper by Dr. Alder and Dr. Phillips. At B.I.S.R.A. we are in a unique position in that the Cam Plastometer, used by these authors in their study of resistance to compression, was transferred to our laboratories in Sheffield in 1952 in order that the work might be continued. Since that time, an extensive programme on twelve commercially important steels has been undertaken. Stress/strain curves in compression have been determined at 900°, 1000°, 1100°, and 1200° C. at natural strain rates of 1.5, 8, 40, and 100 sec.⁻¹. The tests at a strain rate of 100 sec.⁻¹ and on high-strength steels such as the 18 : 4 : 1 type high-speed steel were made possible by designing a new cam and using specimens 0.5 in. high × 0.375 in. in dia.

Although molten glass is still used as the lubricant, we disagree with Alder and Phillips about the effectiveness of various types at different temperatures. In our experience, minimum barrelling during compression is achieved by using the lead borate glass (type A) at 900°–1000° C., Pyrex (type D) at 1200° C., and an Extra-Hard Flint (not specified by the authors) at 1100° C. The waviness of the stress/strain curves referred to by the authors is also evident in all our results, and is attributed to the conflict between strain-hardening and thermal softening due to recrystallization. Alder and Phillips have also referred to the complex manner in which stress varies with temperature and strain rate for copper, aluminium, and mild steel. The situation is even more complex in the case of alloy steels; in fact, for one particular steel (En 52, a silicon-chromium valve steel) the stress at 1000° C. for any specified strain and strain rate is appreciably higher than that at 900° C. In the absence of a detailed investigation of the matter, it is tentatively suggested that the effect is due to the formation of the σ phase.

Attention has been drawn to the fact that high-speed compression tests of this kind are not carried out at constant temperature, owing to the heat developed during deformation. A similar state of affairs exists, however, in hot rolling, for which these yield-stress/strain curves have been specifically determined to enable rolling loads and torques to be calculated.

Mr. G. L. BAILEY,** C.B.E., M.Sc., F.I.M. (Member): I am in considerable doubt as to the validity of the implied assumption in the first paragraph of the paper by Dr. Hundy and Dr. Singer that the presence of internal stresses might be related to inhomogeneity after cold work as measured by hardness variations. I particularly wish to call attention in this connection to the information on p. 404, to the effect that a total reduction of 10% in ten passes causes less inhomogeneity than a reduction of 10% in one pass. The implication might be that to effect a reduction of this order in a number of small passes would produce a material freer from internal stress than effecting the same reduction in large passes. I consider that any such conclusion would be quite contrary to the facts.

I should like to refer to the work of Baker, Ricksecker, and Baldwin,†† who showed that residual stresses and liability to fire-cracking are higher when a bearing bronze is reduced 20% in ten passes of 2% than if it is reduced in two passes of 10%. I think we must accept the fact that the use of light passes to effect a reduction of the order of 10–20% produces more severe internal stresses in a susceptible material than the same reduction in heavy passes. I do not question the authors' findings that inhomogeneity as they measure it is less when light passes are given, and I can only conclude, therefore, that it would be a mistake to regard hardness variations as meas-

* J. A. Brinell, *J. Iron Steel Inst.*, 1901, **59**, 243.

† J. A. Pope and A. K. Mohamed, *ibid.*, 1955, **180**, (3), 285.

‡ G. H. Williams and H. O'Neill, *ibid.*, 1956, **182**, (3), 266.

§ Head, Metal Working Laboratory, British Iron and Steel Research Association, Sheffield.

|| E. Siebel and H. Hühne, *Mitt. K. W. Inst. Eisenforsch.*, 1931, **13**, (3), 43.

¶ British Iron and Steel Research Association, Sheffield.

** Director, British Non-Ferrous Metals Research Association, London.

†† R. McC. Baker, R. E. Ricksecker, and W. M. Baldwin, Jr., *Trans. Amer. Inst. Min. Met. Eng.*, 1948, **175**, 337.

ured by these authors as directly related to the intensity of the internal stresses present in the material.

Dr. D. TABOR*: The paper by Dr. Hundy and Dr. Singer is an interesting one and shows that the authors have taken a great deal of care in their experimental work. My only criticism is in the use of hardness values as a measure of inhomogeneity of deformation. For annealed metals small differences in deformation lead to large differences in the hardness, but for highly worked metals the hardness measurements are quite insensitive. Consider, for example, an annealed copper specimen (D.P.N. 45) which is deformed so that the central elements are deformed 5% and the outer surface by 10% true strain (log strain = 0.05 and 0.10, respectively). The Vickers hardness values will be approximately 65 and 72, respectively, i.e. a difference of about 12%. If the deformation is very much heavier, say 50% true strain in the central elements and 100% true strain at the outer surface (log strain = 0.5 and 1.0, respectively), the Vickers hardness values will be approximately 105 and 107, respectively, i.e. a difference of only 2%.

It seems to me that the authors ought first to correlate the Vickers hardness measurements with the true logarithmic strain of uniformly deformed copper, and then, using this correlation, compare the true strain at the centre of the rolled specimens with the true strain at the outer surface. The difference between these values would, I feel, give a much better measure of the inhomogeneity of deformation. I have tried to do this with the data given, but some of the details, which the authors probably have in their possession, are not available in the paper. It appears, however, from my own inadequate attempts, that the inhomogeneity of strain is little (if any) greater for the deformation of annealed metals than for heavily deformed metals. I should welcome comments from the authors on this point.

Mr. A. J. FIELD,† M.C., B.Sc., F.I.M. (Member): These three papers are of value in illustrating methods of obtaining fundamental data to be applied in the study of hot and cold rolling. The adequate range and consistency of the results gives confidence in their accuracy.

The paper by Dr. Alder and Dr. Phillips on the resistance to deformation in compression of various metals at various temperatures should prove of assistance in the formulation of energy equations for rolling which might assist in pass-setting on existing machines and in the design of new machines. Normally, all the facts that are available in connection with a single flat rolling mill are amperage (for torque and force), gauge, and speed—with, in addition, tension for strip mills—so that the values for metal compression given in the paper, when combined with these, may lead to a fuller understanding of the process.

The paper by Messrs. Leech, Gregory, and Eborall describes an impact tensile test suitable for elevated temperatures, and capable of being carried out at speeds comparable with those of rolling, that should be of assistance in indicating the best hot-rolling temperature range. The contributions to the discussion of this paper by Dr. Hughes and by Dr. Lyons and Mr. Hodierné, showing the effect of repeated torsion tests, form a very interesting supplement, even though, as has been pointed out, the best hot-rolling temperature for Duralumin-type alloys is about 470° C., whereas the maximum torsional plasticity as shown by the curves in Fig. E occurs at 400° C.

In this paper, in the assessment of edge cracks, in view of the semi-circular edges of the test-pieces used, the vertical lines of compressive force through the specimen being rolled would not pass through the edges, leaving these to be deformed mainly by unassisted tensile elongation transmitted from the central body of the specimen, a condition which is conducive to early edge cracking. Square-sided test-pieces might be

expected to give a truer indication of the edge cracking due to rolling.

In connection with the paper by Dr. Hundy and Dr. Singer, information on the relationship between the microhardness value of the material and its tensile strength and elastic limit, as these increase with rolling, would be of interest in attempting to explain the hardness variations reported in the test. It has been found that on progressively cold-rolled sheets, the dynamic or rebound hardness as measured by the Shore scleroscope is proportional to the elastic limit, while an indentation hardness test such as the Brinell test gives values proportional to the tensile strength; the two properties do not run parallel in the early stages of deformation after anneal, the elastic limit increasing the faster. The inhomogeneity of deformation in rolling must in fact be quite limited. It is often said that in the rolling process, the outer layers of the metal are deformed more than the inner, but if this went on progressively, a single plate would be extended into two separate sheets with a central dividing fissure, joined in one place. The greatest difference in layer deformation comes in the early stages of hot rolling. With heavy passes on soft material, the inner layers are "extruded" a little beyond the outer, making the ends slightly convex: in hot rolling hard materials, with necessarily lighter passes, the outer layers are deformed rather more than the inner in the opening passes and form concave fishtail ends with 4 in. concavity on a 12 ft. length as about the maximum difference; this is only some 5%, and as rolling proceeds it diminishes. Micro-examination of longitudinal sections indicates a generally uniform crystallographic extension, while a study by means of wire inserts has shown fairly even deformation in reversed hot rolling.‡ The molecular displacements corresponding to the increased outer-layer hardening observed under some conditions must be of a complex nature.

Mr. EBORALL, Mr. LEECH, and Mr. GREGORY (*in reply*): Dr. Chaston criticizes us for considering the hot working of metals in terms of a simple test for tensile ductility, and suggests that the test is too far removed from practical conditions to be worth while. The trouble about tests of a more practical nature lies in the complexity of the factors involved in hot-working processes. The situation varies from operation to operation, from metal to metal, and from plant to plant, and it would be quite impossible to devise any simulative test which was valid for more than a very limited range of conditions. What has to be done, if any understanding of the behaviour of the metal is to be achieved, is, on the contrary, to attempt to single out relevant properties of the metal itself, which are independent of the machinery used for metal working, to measure them, and to see to what extent, if at all, they affect the behaviour of the metal in actual working operations. This is what we have tried to do. We do not suppose, however, that the property we have measured is the only one relevant to the problem of cracking in working; there are clearly others, quite apart from the question of power requirements for which an approach similar to that of Dr. Alder and Dr. Phillips is appropriate.

In working a metal, the ideal is to arrange for it to be stressed compressively in all three directions, so that the required deformation is produced by the differences between these compressive stresses. Unfortunately, departures from the ideal are bound to take place. For example, not only may there be notch effects due to imperfections in the metal, but in strip rolling there are liable to be tensile stresses at the edges, especially if they bulge, and also in the surface of strip as it leaves the rolls. Similarly, in rod and section rolling, tensile stresses are liable to develop in unsupported regions. In general, it is tensile stresses that cause failure, although of course it will not usually be simple tension that is present. The choice of (approximately) simple tension as a

* Research Laboratory on the Physics and Chemistry of Surfaces, Department of Physical Chemistry, Cambridge University.

† Works Manager, The British Aluminium Co., Ltd., Falkirk.

‡ F. Kasz and P. C. Varley, *J. Inst. Metals*, 1949-50, 76, 407, Figs. 5 and 6, Plate LVII.

test condition is arbitrary, and it may not be the best possible, but the ductility in the presence of tensile stresses under known and standardized conditions seems a reasonable property to measure.

A hot-working process may comprise a succession of fairly rapid deformations, with a pause between during which the metal can recover or recrystallize (e.g. hammer-forging or rolling), or it may consist of one or more slower larger deformations, during which the recovery keeps pace with the deformation (e.g. die-pressing or extrusion). In considering the first type of process, we should certainly not expect to be able to predict the best hot-working temperature from the results of impact tensile tests alone, since, to mention only one thing, the test by itself gives no information about the recovery between blows. As regards the second type, we should certainly agree with Dr. Lyons and Mr. Hodierné about the desirability of testing at the appropriate rate of deformation. In any process, however, the real limitations may be set by the power of the machinery available or the structure developed during working, so that it is necessary to be rather cautious about defining an optimum hot-working temperature.

We were very interested in the accounts given by Dr. Hughes, and by Dr. Lyons and Mr. Hodierné, of results obtained with the hot torsion test. They make out a good case for the test, and Dr. Hughes' observations on the correlation between this test and tube-piercing are especially remarkable. The maximum in turns to failure, with the marked fall as the melting point is approached, which this test reveals for both copper and aluminium, is quite surprising. In reply to Dr. Hughes, we have no results for the impact tensile test on copper at any temperature above 900° C., at which point the elongation and reduction of area are still high, but it seems probable that the behaviour would be similar to that of aluminium.

It seems rather unlikely that the large differences in result between the torsion test and the impact tensile test are attributable mainly to the difference in strain rate. The most significant difference between the two tests is probably that in the torsion test the metal is deformed by a pure shear stress instead of direct tension. Consequently the maximum tensile stress present at a given stage of deformation is only approximately half what it is in the tensile test carried out under similar conditions; failure, therefore, occurs at larger deformations, and such factors as work-hardening, and the concurrent thermal softening which may prevent the amount of work-hardening becoming excessive, are correspondingly more important in determining behaviour in this test. As we point out in the paper, the impact tensile test does not provide much information about softening and recrystallization, and clearly the results of the test have to be considered in the light of other knowledge on these points.

Dr. ALDER and Dr. PHILLIPS (*in reply*): We are sorry that Dr. Chaston is not happy about the effect of friction in our compression tests. It is hard to see what further tests he has in mind to evaluate end friction. The effect of lubrication on the average load required to make a given compression was discussed on p. 83 and attention drawn to the results (Tables II-IV) from comparative tests on cylinders of different diameters. These, and others not reported, show clearly that the effect of end friction on the results was very small. The use of glass lubricants enabled us to compress simple cylinders at elevated temperatures without "barrelling". Tests in which end friction affected the metal flow, as evidenced by "barrelling", were discarded almost without exception.

Possibly Dr. Chaston has in mind the use of specimens with coned ends* or grooved ends.†

Objections to the use of coned ends have been pointed out by Polakowski.‡

Grooved-end specimens were tried, but were rejected in favour of simple cylinders since inhomogeneous compression

tended to occur at the ends as a result of the reduced cross-sectional area.

We are gratified to learn from Mr. Cook that our work has now been extended to cover a range of commercial steels, and to include higher strain rates. We are interested in his observations on glass lubricants, about which there is clearly a great deal to learn.

Dr. HUNDY and Dr. SINGER (*in reply*): It seems to us that the discussion on our paper has two broad aspects: first, the question of the validity of hardness tests as a measure of inhomogeneity, and secondly, the meaning of the results. We discussed our reasons for choosing hardness tests in preference to any other method of measuring inhomogeneity in our paper, but we are the first to admit that this method is not perfect; especially as the results may be affected by phenomena such as the Bauschinger effect mentioned by Professor O'Neill and by Mr. Wistreich. An X-ray method might have been preferable for this reason, but was felt to be much too lengthy if we were to cover a reasonably wide range of variables in the limited time at our disposal.

We agree with Mr. Wistreich that, in certain circumstances, the grid technique can give most useful results; it is possible, however, to envisage a case where an internal reversed shear takes place which hardens the metals without affecting the grid. We felt this to be an especially serious drawback in the case of rolling, where the direction of the frictional drag is reversed as the metal passes through the roll gap. In addition, as Mr. Wistreich admits, the technique is very tedious.

Dr. Tabor raises the point that the relation between strain and hardness is not linear and that differences in strain in a work-hardened metal would be more difficult to detect than in a soft one. This, of course, is perfectly correct, and slight inhomogeneity of deformation in some of our more heavily worked samples might not be revealed. We have, however, replotted some of our results on the basis of true strain inhomogeneity, as suggested by Dr. Tabor, and our conclusions pertaining to the major inhomogeneity are not changed by this. We still find, for example, that the major inhomogeneity in copper decreases very markedly as the reduction is increased up to 14%, where it disappears, and that the effects of frictional conditions, &c., remain exactly as stated in the paper. The only effect of this method of presenting the data is that the straight lines in most of the diagrams relating inhomogeneity to reduction become slightly curved and the actual inhomogeneity figures are changed somewhat.

Turning now to the question of the meaning of our work. We agree with Dr. Chaston and Mr. Wistreich that our results apply only to the particular metals and conditions investigated: they are not necessarily of general application. We agree that plasticity theory suggests that a work-hardened metal will deform more inhomogeneously than a soft one, but, according to our ideas, this applies only to the secondary inhomogeneity, which is a geometrical effect, and not to the major inhomogeneity, which is due to friction. In fact, our wire-drawing tests indicated that the secondary inhomogeneity did become more pronounced as the drawing reduction was increased, and this can be taken as supporting Mr. Wistreich's point.

As Mr. Bailey points out, there can be no simple relation between residual stresses in a metal and the inhomogeneity of deformation as revealed by hardness or other tests. Residual stresses can arise from strain differences of an elastic order of magnitude only, and therefore cannot really be indicated directly by measurements of inhomogeneity. The inhomogeneity of deformation, however, is bound to have a pronounced effect on the residual stresses, even though they are not related directly, and we therefore think that our work on inhomogeneity may be of some value in this connection. As an example of this we would like to quote some more recent work by one of us,§ which showed that, at light rolling

* E. Siebel and A. Pomp, *Mitt. K. W. Inst. Eisenforsch.*, 1927, 9, 157; 1928, 10, 55.

† N. Loizou and R. B. Sims, *J. Mechanics Physics Solids*,

1953, 1, 234.

‡ N. H. Polakowski, *J. Iron Steel Inst.*, 1949, 163, 250.

§ B. B. Hundy, *ibid.*, 1955, 179, 23.

reductions, the surface stresses in copper strip were compressive and became smaller as the reduction was increased, while the comparable stresses in rolled mild-steel strip were tensile and increased in magnitude as the reduction was raised. These results can be compared with the results of our hardness tests, where we found that copper showed surface hardening at light reductions which decreased as the reduction was increased, while steel showed no surface hardening at even the lightest reductions. Other tests in this paper also suggest that the work on residual stresses by Baker, Ricksecker, and Baldwin* is strictly applicable only to the particular material used by them and to their particular rolling conditions and should not be taken as being generally applicable.

Discussion

Corrosion of Aluminium Alloys†

Dr. U. R. EVANS,‡ M.A., Sc.D., F.R.S., F.I.M. (Member): Dr. Champion's reassuring review will be welcomed in many quarters, but I earnestly hope that his "comfortable words"—the truth of which may in the main be accepted—will not discourage further work on stress and corrosion, since our knowledge is still seriously incomplete.

Dr. Champion—with distinguished support—would like to restrict the term "stress corrosion" to cases where corrosion and stress, operating together, produce more damage than when they operate separately. If this restriction is accepted, it should not blind us to cases where ordinary intergranular corrosion, acting without high stress but over long periods, weakens the material so that when, later, a stress, which at the outset could have been withstood, is momentarily applied, fracture occurs. Such fracture will be ascribed, rightly, to mechanical failure, and the part played by corrosion may never be brought to light. Perhaps some failures which in the past have been attributed to the designer having under-estimated the forces to be withstood, or perhaps to the manufacturer having supplied material below the specified strength, may in fact be due to neither cause; it is difficult to prove this, but equally difficult to disprove it.

Again there is layer corrosion—which has caused anxiety in several countries of late. This is presumably excluded from Dr. Champion's select company of genuine stress-corrosion failures, since the stress is mainly generated by the corrosion itself. If once attack starts along lamellae, either at the sheared end of a plate, or at a place where the surface layers have been cut away for some legitimate purpose, the expansional forces due to the voluminous character of the corrosion products, will lever up the unchanged aluminium layers and open up a path for further advance of the corrosion.

If it is a fact that stress-corrosion and allied phenomena are rare in service, this must be attributed to the vigilance of the inspectorate and the maintenance staff, and to the restraint of the designer, who deliberately refrains from using materials possessing the mechanical properties which he would choose; occasionally the use of a strong material has been abandoned on account of its proneness to stress corrosion. However short may be the list of materials definitely convicted of corrosion cracking (and continued research may add to that list), the situation must be regarded as unsatisfactory whilst the list contains some of the strongest and most attractive of our light alloys.

It is often stated that cladding and spraying provide the remedy, and it is claimed that cladding protects uncovered metal over considerable distances. This may be true where

We agree with Mr. Field that the extension of the surface of rolled sheet cannot exceed that of the centre by more than an elastic order of magnitude, if the strip is to remain in one solid piece, and this would give a very limited degree of inhomogeneity. We believe, however, that the difference in hardness through the sections tested by us is due to a difference in shear strain undergone by the various parts of the strip and these strains are not limited to the same extent.

In answer to Dr. Chaston's point about the details of the wire-drawing die shape, we regret that we have little more information than we gave in the paper. We can add, however, that the dies were made to be as nearly conical as possible, with a short parallel portion.

the surface is definitely wet with strong salt solution, but less true where the surface is only moist, and the moisture only slightly conducting. A concentrated salt-spray test is not really a severe test for clad material; dilute salt solution, followed by intermittent spraying with water, might prove more drastic, and probably more consonant with some service conditions. Chloride is not seriously used up during corrosion, and the plan of adding it continuously appears to be unrealistic.

Even when it is continuous, cladding does not always protect the face, notably when clad copper-containing alloy is exposed to heat, permitting diffusion of copper outwards along grain boundaries, which become cathodic with respect to the interior. Corrosion of the cladding then follows, as shown in Fig. A (Plate LXXIX); Fig. B (Plate LXXIX) illustrates the subsequent disintegration of the alloy below. These examples are taken from aircraft, the heat emanating from the engine, but the phenomenon has been repeatedly produced in the laboratory.

Stress corrosion and layer corrosion generally result from under-ageing. The ill effects of over-ageing are generally recognized, but with some alloys at least this will be discovered from the measurement of tensile strength, which diminishes on over-ageing. Under-ageing, however, seems to have much less effect on the strength of the uncorroded material, though it increases the tendency to lose strength through corrosion; in the case of alloys where this is true, under-ageing is far more insidious than over-ageing, and it would seem that more attention should be given, in the otherwise excellent literature on heat-treatment provided by the aluminium industry, to the fact that ageing is really a leap over a dangerous ditch, where the consequences of leaping insufficiently far may be serious. Complaints of stress corrosion or layer corrosion from a number of sources in recent years are believed to have their origin in under-ageing. It has been stated by American writers that the increasing size of pieces requiring heat-treatment is making it ever more difficult to preserve correct conditions throughout the piece.

Dr. H. K. FARMERY,§ M.A. (Junior Member): Dr. Champion's paper provides a summary of the stress-corrosion properties of aluminium alloys which must be welcomed by producers and potential customers alike. However, there do appear to be several points upon which agreement is not unanimous.

In the first place there is no point in closing our eyes to any failures that occur when structures are stressed beyond 75% of the material's proof stress and simply attributing them to

* R. McC. Baker, R. E. Ricksecker, and W. M. Baldwin, Jr., *Trans. Amer. Inst. Min. Met. Eng.*, 1948, **175**, 337.

† Joint discussion on the papers by N. P. Inglis and E. C. Larke (*J. Inst. Metals*, this vol., p. 117), and by F. A. Champion (this vol., p. 385).

‡ Emeritus Reader in the Science of Metallic Corrosion, Cambridge University.

§ Fulmer Research Institute, Ltd., Stoke Poges, Bucks; formerly Metallurgy Department, Cambridge University.

creep. Internal stresses are very likely to be set up during fabrication unless extreme care is taken in machining and assembly, especially with the high-strength alloys, and these stresses, coupled with those applied during service, will almost certainly reach the proof stress. This stress need not be maintained for any length of time, since highly susceptible alloys, under certain conditions, can fail in under a minute after application of the load. For this reason I feel it would be dangerous to limit laboratory tests to this figure of 75% of the 0.1% proof stress. Moreover, if such a restriction applies to condition (3) on p. 386 of the paper when investigating possible stress-corrosion failures, it may lead to a faulty diagnosis. Similarly, care should be exercised with condition (1), since some alloys are known to be mechanically weak at the grain boundaries after a particular heat-treatment and straight-forward mechanical failure will then produce an intergranular fracture.

Regarding the mechanism of cracking, I should like to mention some experiments carried out in Dr. Evans's laboratory at Cambridge, which seem to conflict with the film-cracking theory. A specimen of susceptible aluminium-7% magnesium alloy was stressed under total immersion conditions in sodium chloride solution and allowed to crack halfway through its cross-section before cracking was halted by an impressed current (normal life 15 min.). After $\frac{1}{2}$ hr. the current was stopped, but cracking did not continue, although 15 hr. later fresh cracks appeared elsewhere. A similar specimen was allowed to crack through one-third of its cross-section before arrest by an impressed current, which was stopped after 30 min. Although an additional light load was added, which would certainly rupture any film at the base of the crack, the specimen remained unbroken after 48 hr. These experiments led us to assume that maintenance of acidity at the base of a crack, by anodic action, is far more important than the cracking of any films.

In Section IV (p. 327) on "Environment", it is stated that oxygen is necessary for stress-corrosion cracking; now, although it is generally true to say that the hydrogen-evolution reaction on aluminium in near-neutral solutions is very sluggish, if one removes the thick oxide film normally present on the surface, this does not necessarily apply—at least in the early stages. Thus in the case of aluminium-7% magnesium alloy in the susceptible condition, if this thick film is removed by some suitable reagent, e.g. aluminium chloride solution, specimens will crack in completely deaerated sodium chloride solution. I think one would expect similar cracking to occur even with alloys carrying the thick oxide, if they were unfortunately in contact with a noble metal on which the evolution of hydrogen was an easy process.

Highly aged aluminium-7% magnesium alloy, e.g. aged 50 days at 150° C., which is extremely notch-sensitive, can fail in about 15–30 sec. when loaded at 80% of its proof stress if this thick film is removed. It would be interesting to know whether the high-strength aluminium-zinc-magnesium alloys, which can also be highly notch-sensitive, would fail in a similar time if so treated, since high stresses for such short periods undoubtedly occur in aircraft.

This tendency to notch-sensitivity in highly aged aluminium-7% magnesium alloy should be borne in mind in relation to lines 12–15 of the first column on p. 389 of the paper; for agglomeration to occur in any reasonable time, the ageing temperature should be much higher than 125° C.

I am rather surprised that Dr. Champion considers an increase of four times in the loss of strength of an alloy between stressed and unstressed conditions, as given in Table II (p. 389), to be only a moderate effect. Lower down in the same column, additions of copper, manganese, or chromium are stated to minimize the susceptibility to stress corrosion of aluminium-zinc-magnesium alloys; this may be true for sheet, but I think a word of warning should be given about the increased possibility of cracking in the short transverse direction in extrusions and forgings.

Referring to internal stresses in the section on "Protective Measures" (p. 390), it may be pertinent to mention the work of Richards,* in which it was found that the level of internal stresses in material quenched into water after solution-treatment was very much higher if such material had previously been anodized.

Finally, I should like to ask Dr. Champion if he has any evidence that pure aluminium cladding remains anodic to Duralumin-type alloys under all conditions of heat-treatment, especially when the alloy is over-aged (assuming no diffusion of copper through the cladding).

MR. E. A. G. LIDDIARD,† M.A., F.I.M. (Member): The paper by Dr. Inglis and Mr. Larke provides useful data on the subject of corrosion-fatigue of light alloys, information on which is meagre. The results obtained with the painting scheme used by these investigators are encouraging, but since the speed of the test machine is such that the tests reported have extended over only 14 days at most, it would be unwise to assume without further evidence that painting offers a permanent protection. Experience at the Fulmer Research Institute has been that painting is not entirely successful in preventing either stress-corrosion or layer-corrosion in H15-WP alloy, and we agree with Dr. Champion's findings that cladding with anodic coatings of aluminium or aluminium-zinc alloys is more effective than paint for this purpose. It seems unlikely, therefore, that painting can always be relied upon to provide permanent protection against corrosion-fatigue. Some paints or painting schemes may be more effective than others, but it is unfortunately rarely possible to define these more precisely than by reference to proprietary products.

It is hoped that Dr. Inglis and Mr. Larke will provide further data on the fatigue behaviour of painted specimens which have been subject to the normal hazards of service, including ageing, long contact with the corroding medium, exposure to sunlight, scratching, or other superficial damage.

In addition to being an interesting summary of existing knowledge and of his own experience, Dr. Champion's paper is both stimulating and controversial. In the laboratory investigation of the interaction of stress and corrosion, it is important to find out whether corrosion damage is increased or accelerated by the presence of stress; the definition quoted by Dr. Champion is useful in emphasizing this point and was primarily intended for research workers. In my opinion, Dr. Champion is asking rather too much from engineers in demanding such nice distinctions in considering cases of failure, or in deciding which alloy can or cannot be used without protection from the combined action of stress and corrosion. Apart from the definition itself, the criteria that Dr. Champion applies before he will admit stress-corrosion in aluminium alloys are exacting. The failure must be intercrystalline and the alloy must be shown by laboratory tests in which the stress is limited to 75% of the 0.1% proof stress to corrode more rapidly in the presence of static stress.

The vast majority of failures of aluminium alloys by stress and corrosion are, of course, intercrystalline, but many other forms of stress-corrosion failure are transcrystalline, e.g. those in magnesium and its alloys in distilled water and austenitic stainless steels. I should hesitate to say that the transcrystalline type of corrosion associated with a banded structure and illustrated in Fig. C (Plate LXXIX) is not accelerated by stress, particularly since we have found ‡ that directionality of structure can accelerate stress corrosion when the stress is at right angles to the plane of directionality. Corrosion-fatigue is, of course, transcrystalline, as illustrated by Dr. Inglis and Mr. Larke, and it is not quite clear where the practical distinction between corrosion-fatigue and stress corrosion can be drawn, bearing in mind that service stresses are very rarely entirely static.

The limitation to 75% of the 0.1% proof stress seems even more unrealistic in that most engineering materials must be expected to be stressed locally well above their yield point

* G. W. Richards, *Metal Ind.*, 1955, 86, (4), 63.

† Director, Fulmer Research Institute, Ltd., Stoke Poges, Bucks.

‡ E. A. G. Liddiard and (Miss) W. A. Bell, *J. Inst. Metals*, 1953–54, 82, 426.

by riveting, caulking, bending, &c. In other cases of stress-corrosion, e.g. caustic embrittlement and attack by sodium nitrite on steels, attack is in practice confined to those areas where the material has been deformed by cold-working operations. It is for this reason that I consider that any stress-corrosion testing carried out with the object of guiding engineers and designers, should include tests on specimens which have been permanently deformed or stressed up to the 0.1% proof stress.

Dr. Champion's preoccupation with strict definitions, as distinct from practical considerations, is exemplified by the phrase in column 1, p. 389, of his paper, which reads "... since it was admitted that the stress conditions in the stress-corrosion tests conformed to commercial practice rather than to good testing technique". Tests intended to determine liability to failure in practice should surely conform to practical conditions, although such tests may be unhelpful to the research worker in studying the mechanism of failure.

The mechanism suggested by Dr. Champion to account for stress corrosion in aluminium alloys may well be the correct one, but a purist might argue that his explanation does not demand the *simultaneous* action of stress and corrosion and therefore that this is not strictly a case of stress corrosion as defined. The effects of rupture of the film and stress concentration followed by re-forming of the film could in theory be produced by the alternate application of stress and corrosion with a frequency equal to that of the steps in the idealized stress-corrosion curve in his Fig. 5 (p. 387).

Another explanation, which to me is more satisfying, is that the application of stress (whether static or dynamic) causes a certain localized disarray of atoms which may be either at grain boundaries or slip planes, depending on the metal and the type of stress. Such disarray slightly increases the chemical activity, and when the corrosive environment is such that this markedly affects the equilibrium or kinetics of the corrosion reaction, attack is concentrated at these points and continues faster and deeper as further disarray results from the increasing stress concentration. Corrosive reactions which occur strongly are little affected by small changes in activity and media that attack rapidly do not therefore cause stress-corrosion. The most striking effects are obtained in condi-

tions in which small changes in activity become significant, and sometimes even in cases where no apparent corrosion occurs in the absence of stress. Film formation may well play an important part, but it is not essential to the mechanism. A mechanism of this type covers, in addition, attack by molten metals, e.g. mercury on brass, and can explain differences

between static and alternating stress when the maximum disarray can change from the grain boundaries to the slip planes. It demands, however, the application of a stress sufficient to cause a very small localized distortion.

In his excellent and otherwise comprehensive review of stress-corrosion in aluminium alloys, Dr. Champion has not mentioned that the relative susceptibility of different alloys may change in different media. This point is illustrated in Table A below, giving results of tests on aluminium-copper-magnesium and aluminium-zinc-magnesium alloy test-pieces taken from across the flash-lines in experimental forgings.

It will be seen that, sprayed in 3% sodium chloride solution, the aluminium-copper-magnesium alloy (D.T.D. 364) shows much greater susceptibility to stress corrosion than the aluminium-zinc-magnesium alloy (D.T.D. 683), whereas in a normal rural atmosphere the reverse is true.

Dr. T. P. HOAR,* M.A., F.R.I.C., F.I.M. (Member): The reduction of the air fatigue strength of aluminium alloys caused by anodizing, noted by Dr. Inglis and Mr. Larke, is probably caused by slight grain-boundary attack during anodizing. Lacombe† has illustrated the heterogeneity found in the anodized oxide film at parts corresponding to the metal grain boundaries in all but the purest aluminium; it is accompanied by "nicking" of the metal grain boundaries at the metal/film interface. Either phenomenon might be expected to decrease the fatigue strength of anodized aluminium alloys.

If definitions are needed for "stress corrosion" and "stress-corrosion cracking", I suggest:

Stress Corrosion.—Corrosion that is accelerated by static stress.

Stress-Corrosion Cracking.—Cracking that is produced by the conjoint (though not necessarily simultaneous) action of static stress and corrosion, but that cannot be produced by either acting alone.

However, there are evidently so many different phenomena in the general field that I am doubtful whether much is achieved by the adoption of rigid definitions: it would be clearly wrong to dismiss a new kind of fracture as *not* stress-corrosion cracking because its details fell slightly outside a formal definition.

Dr. H. SUTTON,‡ C.B.E., F.R.Ae.S., F.I.M. (Member of Council): Dr. Champion has given a good general review of the position for which all interested in the subject will be grateful.

There is increasing use of the very strong wrought alloys in aircraft in hydraulic equipment under high stresses applied over long periods during which there is a high mean tension stress and some fluctuations of stress around the mean stress.

Fabrication and handling of these very strong alloys necessitate special techniques and precautions, and in these matters there has been much advancement. There is always a risk, however, of leaving locked-up stress in an engineering structure, and it is difficult to ensure that these stresses do not at any place exceed any particular level. Stress-cracking is sometimes encountered, but in most of the cases known to me it has fortunately occurred before the particular part has reached service. There is much evidence that corrosion exerts an influence, and it is not surprising that engineers and others experiencing these troubles are in the habit of referring to such cases as "stress-corrosion" failures. Up to the time of substantial or even complete fracture, the pieces frequently show little, if any, deterioration of the static-stress characteristics as usually examined. The 1945 definition of stress-corrosion to which Dr. Champion has appropriately referred goes a long way and seems to have served a useful purpose. It does not in itself, however, suggest risk of the kind of stress-cracking which can occur in particular materials and circumstances even in the absence of visible corrosion as known to the man in the street. It is hoped therefore that increased attention and effort will be given to stress-cracking phenomena and avoidance of stress-cracking, by all concerned.

TABLE A.—Results of Stress-Corrosion Tests on Aluminium Alloys.

Medium	Alloy	Stress, tons/in. ²	Life, days	Mechanical Properties, Corroded Unstressed for:	
				Days	U.T.S., tons/in. ²
<i>Tests in Direct Tension</i>					
Salt spray	D.T.D. 364	$\left\{ \begin{array}{c} 20 \\ 16 \\ 6 \end{array} \right.$	$\left\{ \begin{array}{c} 2 \\ 3 \\ 7 \end{array} \right.$	4	26.6
	D.T.D. 683	$\left\{ \begin{array}{c} 25 \\ 20 \end{array} \right.$	$\left\{ \begin{array}{c} 17 \\ 33 \end{array} \right.$	16	34.4
<i>Bend Tests</i>					
Rural atmo- sphere	D.T.D. 364	$\left\{ \begin{array}{c} 24 \\ 20 \end{array} \right.$	$\left\{ \begin{array}{c} 180, 161 \\ 174, 199 \end{array} \right.$		
	D.T.D. 683	$\left\{ \begin{array}{c} 25 \\ 20 \end{array} \right.$	$\left\{ \begin{array}{c} 27, 147 \\ 73, >240 \end{array} \right.$		

tions in which small changes in activity become significant, and sometimes even in cases where no apparent corrosion occurs in the absence of stress. Film formation may well play an important part, but it is not essential to the mechanism. A mechanism of this type covers, in addition, attack by molten metals, e.g. mercury on brass, and can explain differences

* Department of Metallurgy, Cambridge University.

† P. Lacombe, *Trans. Inst. Metal Finishing*, 1954 **31**, 1.

‡ Director of Materials, Research and Development (Air), Ministry of Supply.

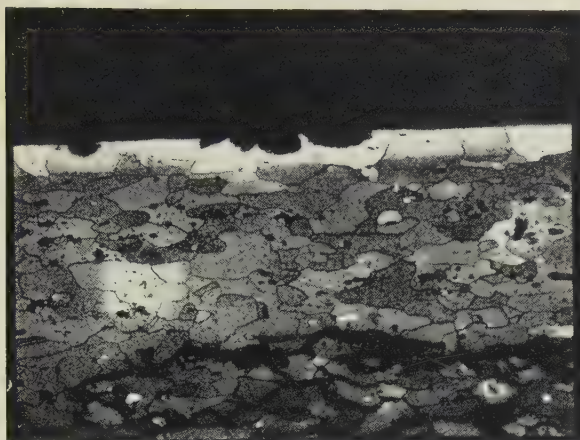


FIG. A.—Pitting of cladding with grain boundaries unattacked, probably due to diffusion of copper through the cladding either during initial heat-treatment or subsequent exposure to heat of engine and the setting up of electrochemical corrosion cells. Etched with Keller's reagent. $\times 250$.

Reduced by $\frac{1}{4}$ in reproduction.

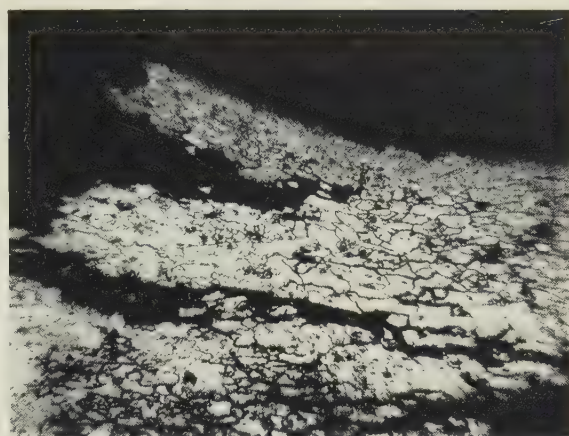


FIG. B.—Illustrating subsequent disintegration of underlying alloy, which has undergone both intergranular and lamellar corrosion. Unetched. $\times 200$.

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FIGS. A and B.—Examples from Aircraft of Corrosion of Clad Aluminium-Copper Alloy Exposed to Heat.
(*H. K. Farmery cited by U. R. Evans.*)

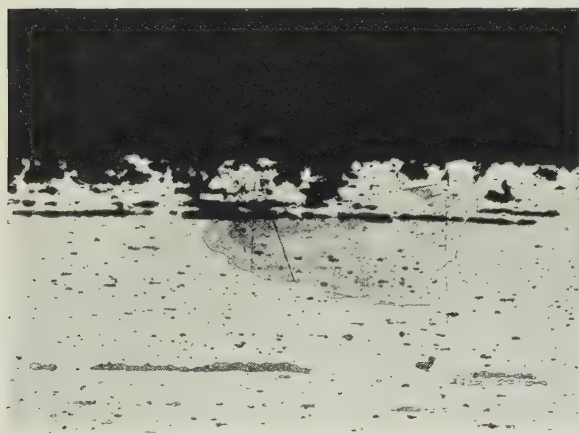


FIG. C.—Transcrystalline Layer-Type Corrosion in Aluminium-2% Copper-1% Magnesium Alloy Exposed for 3 Years at Sheffield. $\times 100$. (*E. A. G. Liddiard.*)

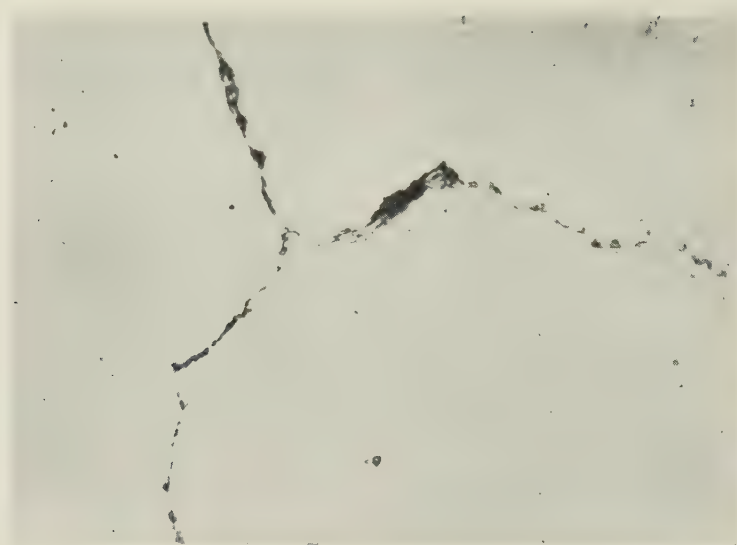


FIG. E.—Grain-Boundary Constituent in Weld-Metal Specimen Containing Essentially 93% Copper with 7% Aluminium, Water-Quenched from 600° C. Unetched. $\times 1800$. (*Shedden and Pumphrey.*)



FIG. F.—V-shaped Type of Precipitate in a 58.7% Copper-41.3% Zinc Alloy Transformed Isothermally at 205° C. for 93 hr. Etched in ammoniacal ammonium persulphate. $\times 1300$. (*Garwood's reply.*)

The paper by Dr. Inglis and Mr. Larke is an important one and forms a most welcome addition to available information on the protection of light alloys in relation to corrosion-fatigue. As pointed out by the authors, much of the published data relates to alloys of the Duralumin type. The type of alloy tested in the work under discussion is widely used, and the results now presented are likely to be of interest and service to a vast field of users and potential users of light alloys, as well as to those concerned with the manufacture and supply of light alloys for various purposes. We live in an age in which there is an increasing need to know about the performance of materials under conditions bearing some relationship to conditions of use. Although corrosion-fatigue studies of the kind now before us have to be made under arbitrarily chosen conditions, they are valuable and yield information such as can lead to advances in the fields of the metallurgist, of the corrosion specialist, and in the broader and

sealing. Investigators studying matters of this kind never include in their programmes all the variables and conditions which can and do arise in the minds of their more interested readers, as the late Mr. Gerard and I discovered when we gave a paper on the corrosion-fatigue of Duralumin to the Institute in 1935.* Gerard and I used a fine spray of 3% sodium chloride as corroding agent for the test lengths of our corrosion-fatigue specimens, but I would not plead that other investigators should use precisely the same conditions. It is probably a good thing that somewhat different conditions should be used in these relatively early days of studies in this field. Looking back to the work of Gerard and myself, it seems to me that one of the more intriguing observations then recorded was that Duralumin anodized by the original Bengough-Stuart process and then varnished with a synthetic resin (stoved) gave higher corrosion-fatigue stress ranges at 10 million and 50 million cycles' endurance than the normal

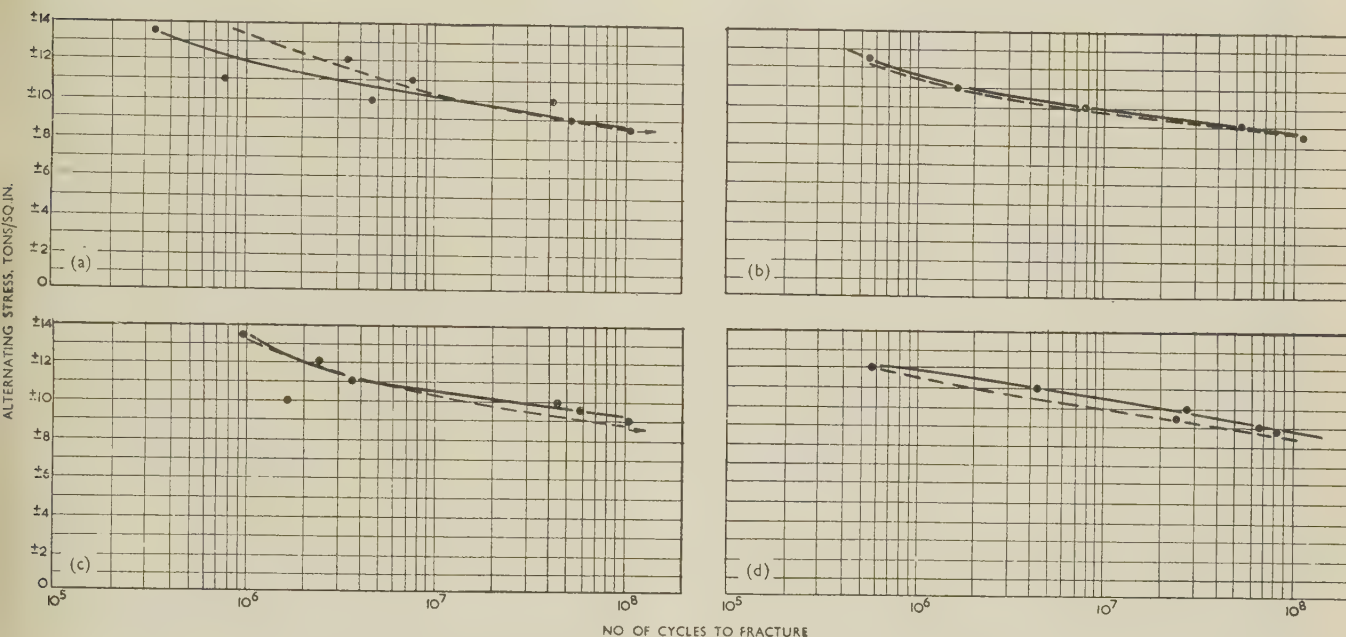


FIG. D.—Corrosion-Fatigue Tests on H10 Alloy. (For key see p. 558.)

ever-broadening fields of service in which light alloys are finding application. The fatigue and corrosion-fatigue tests on unprotected material emphasize the differences in the effects of the various kinds of water used under the conditions of the experiments. If the results are considered in relation to stress, e.g. at ± 6 tons/in.², the endurance in distilled water was thirty times as long as in the 3% sodium chloride solution.

The authors' conclusions on the effect of anodizing in relation to their material and method of anodizing are fully justified by their results. In considering ordinary fatigue tests in the laboratory atmosphere, it is important to bear in mind that not only the material and the manner of anodic treatment have an influence, but also the subsequent sealing treatments of the films. Several investigators have found that the type of anodic treatment that results in very hard, abrasion-resistant, and relatively thick anodic films causes a very considerable reduction in the Wöhler range of a strong wrought aluminium alloy of the D.T.D. 364B type. If, however, the pieces treated by one such process were given film-sealing treatment in a boiling dichromate solution after anodic treatment, the Wöhler range was found to be restored to a value within 10% of the semi-range for 10 million cycles' endurance. It would be of interest to know whether the authors have made any fatigue tests on sulphuric-anodized H10 alloy without

air-test fatigue ranges of the same material in the unprotected condition.

It is worth while to present fatigue and corrosion-fatigue graphs as the authors have done. The shapes of the curves are always of interest. No doubt the originals were much larger than the reproductions, and it is rather a pity that the latter were not printed on a somewhat larger scale.

While the fatigue properties of light alloys as used in service are often greatly affected by mechanical-engineering handling, and design and method of assembly, and frequently more so than they are by the initial surface treatments, it is important that the best advantage should be taken of protective treatments in order that fatigue-resistance of the assembly shall be preserved. In that connection, this paper is a worthy contribution.

Dr. INGLIS and Mr. LARKE (*in reply*): Mr. Liddiard's remarks regarding the length of time over which a special painting treatment may serve as a protection against corrosive attack, are most pertinent. In fact, the question had been anticipated, as the same point was raised by the Institute's referees when the paper was submitted. Tests were therefore put in hand, before discussion of the paper, to throw some preliminary light on this matter. In this work specimens of the H10 alloy were prepared and painted in exactly the same

* I. J. Gerard and H. Sutton, *J. Inst. Metals*, 1935, 56, 29.

manner as described in the paper, afterwards being tested as follows (see Fig. D) :

- (a) Exposed to an industrial atmosphere for 20 weeks, after which the fatigue strength was determined in air.
- (b) As (a), but tested in the presence of the 3% NaCl solution.
- (c) Exposed to salt spray for 20 weeks, after which the fatigue strength was determined in air.
- (d) As (c), but tested in the presence of the 3% NaCl solution.

While we realize that 20 weeks is not a sufficiently long period to warrant drawing a firm conclusion regarding the effect of the ravages of time, the broken-line curves included in the diagrams, which refer to the fatigue strength of the material determined within a week or so of painting, indicate that a careful painting treatment may provide a satisfactory measure of protection. In this connection, Mr. Liddiard may like to know that a similar investigation involving a two-year period of exposure to an industrial atmosphere has begun.

It is gratifying to note Dr. Sutton's remarks regarding the value of our work, and his view that the data presented will have considerable value since they cover a widely used type of alloy. We have also noted Dr. Sutton's remarks regarding the effect of anodizing *without* subsequent sealing and hope, shortly, to have fatigue data available relating to the H10 alloy so treated.

Dr. Hoar suggests that slight grain-boundary attack during anodizing may be responsible for the reduction in fatigue strength, compared with that determined for non-anodized specimens. It is true that during our microscopic examination of the anodized specimens defects and discontinuities were observed in the anodized layer itself, and it was thought that these might act as "stress raisers" during the subsequent alternating-stress tests and so cause the reduction in fatigue strength actually found. We did not observe any grain-boundary attack as a result of the anodizing process, but it is only fair to record that no study was made of the geometry of the observed defects and discontinuities in the anodized oxide layer and the relation, if any, of these with grain boundaries.

Dr. CHAMPION (*in reply*) : I am grateful to the contributors to the discussion for their most interesting comments on my paper, although I must disagree with some of these. It is argued that the definition of stress corrosion and the testing techniques which I advocate are too restricted and too far removed from service conditions. I still feel, however, that research on stress corrosion or the *ad hoc* investigation of service failures both necessitate : (a) analysis and classification of service conditions where, as often, these are complex, and (b) a testing technique based on that analysis to give a clear answer on the specific point to which the particular test is related. The failure of rivets quoted from p. 389 by Mr. Liddiard provides a good instance of (b), as I believe he would have agreed if he had looked at the earlier discussion to which reference was made.* Having separated and investigated the causes of failure, they can then be reassembled to give the complete picture, and this may well need to be presented in a simplified and less accurate form to Dr. Sutton's "man in the street". Thus, investigation of stress corrosion can proceed simultaneously with that of simple intercrystalline corrosion, layer corrosion, &c. In my experience, layer corrosion is an alternative to stress corrosion, depending on the condition and composition of the alloy. There is usually no difficulty in detecting the part played by intercrystalline corrosion in a fracture which is eventually mechanical, as suggested by Dr. Evans, but it may well be difficult to establish whether stress corrosion has occurred. In this connection, I would remind Dr. Farmery that I regard diagnosis of stress corrosion in a service failure as dependent on all three of the observations given on p. 386 and not on one only, such as the first one which he quotes.

Dr. Farmery and Mr. Liddiard favour testing at stresses well above 75% of the proof stress in order to obtain failure more readily in the laboratory. I repeat that high stresses

have probably been largely responsible for making laboratory tests too severe in relation to service experience and for reducing reliability, both of which may result in unjustifiable condemnation of a desirable alloy. However, I have pointed out (pp. 385-386) that in appropriate cases and with appropriate precautions, higher test stresses are permissible.

The discussion has indicated that no generally acceptable theory on the mechanism of stress corrosion of aluminium alloys is yet available, and I would make the following comments on the alternatives proposed. Mr. Liddiard prefers to consider the nature and the mechanism of the fracture of all metals, whereas I feel that a better prospect of progress is offered by considering more restricted classes first. Then, when a satisfactory theory for aluminium alloys has been achieved, its application or relation to other metal systems and to the more ambitious idea of a general theory can be considered. Thus, I feel that Mr. Liddiard's observation that stress-corrosion in other alloys is not always intercrystalline, merely confuses the issue and, with regard to his comments on Fig. C (Plate LXXIX), I note that when that figure was first published, Mr. Liddiard stated quite definitely † that "no case of stress-corrosion failure was observed in this material", and that carries much more weight with me than the conjecture that he now makes that stress corrosion *might* be obtained in this material if the stress were normal to the direction of extrusion. The mechanism proposed by Mr. Liddiard appears to ignore the importance of the electrochemical relations of phases at the grain boundary and the experimental evidence for the steps in my idealized corrosion/time curve. With regard to Dr. Farmery's proposals, I find it difficult to visualize sufficiently localized acidity to account for the observed character of the failures, but if the geometrical conditions left at the cessation of corrosion (on application of cathodic protection) are not such as to cause the highly localized plastic flow under applied stress, and if the protective film formed by cathodic protection prevents further development by corrosion of a notch at that point, then that stress-corrosion crack would not be expected to proceed on removal of the cathodic protection. Hence, I do not consider that Dr. Farmery's observations are at variance with the theory which I have proposed.

I agree with Dr. Evans on the desirability of testing protection by cladding under a wide range of conditions, but would remind him that the efficacy of cladding has been confirmed by extensive service experience under a wide range of conditions, especially with the HC14 and HC15 type of product. I agree that the cladding must have adequate thickness in relation to the thermal treatments to which it is to be subjected, and that where repeated heating in service is unavoidable, cladding cannot be relied upon as the sole protection, but that heat-resisting paints must be applied over it. Effective protection by cladding or metal spraying allows the composition and heat-treatment of the alloy to be chosen for optimum mechanical properties and economical and efficient production. Where such protection cannot be used, these choices must also depend on corrosion effects and, as Dr. Evans has mentioned, more prolonged ageing may be necessary in these cases even though this may mean consequent loss of production capacity, increased costs, and perhaps less attractive mechanical properties.

In reply to Dr. Farmery's final question, I do not know of potential or current measurements covering these wide conditions, especially when coupled with the ambiguous term "Duralumin", but I would reiterate that I know of no case, in laboratory tests or service, of stress corrosion of copper-bearing, zinc-free, aluminium alloys clad with pure aluminium.

In considering Table II, I would ask Dr. Farmery to bear in mind the very small diameter and the long term of exposure of these wires : I still regard the term "moderate" to be appropriate. I agree that further work on the composition of aluminium-zinc-magnesium alloys is required.

I thank Mr. Liddiard for pointing out that the relative corrosion-resistance of different alloys is dependent upon the corrosion conditions and for providing specific information on stress corrosion in this connection.

* *J. Inst. Metals*, 1946, **72**, 663.

† *Ibid.*, 1953-54, **82**, 639 (reply to discussion).

Discussion

Transformations in Copper Alloys*

Mr. D. LLOYD THOMAS,† B.Sc. (Member): With reference to Mr. Garwood's paper, I would draw attention to the apparent similarity between the structures he obtained at low transformation temperatures and those developed during the early stages of transformation of eutectoid copper-aluminium alloys in the region of 450° C. May it be that a bainitic transformation occurs in these copper-aluminium alloys?

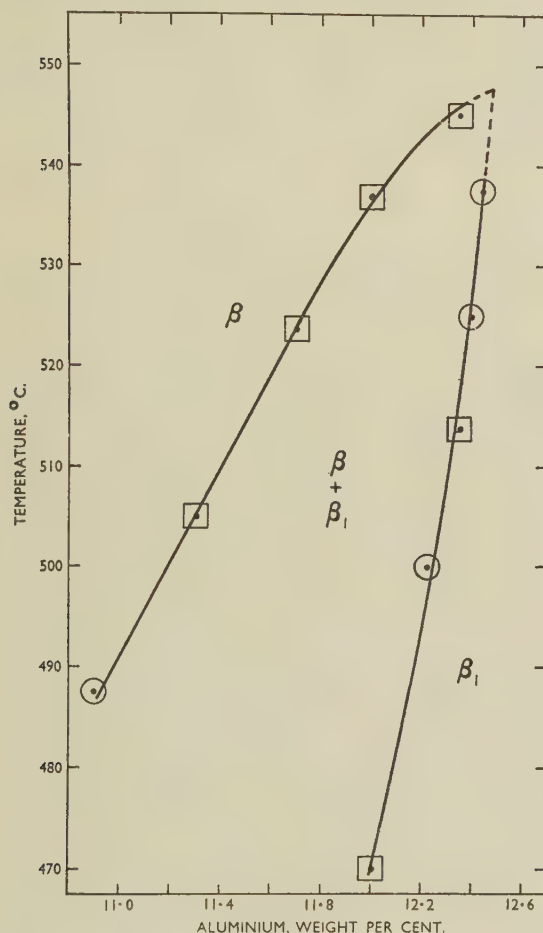


FIG. A.

My further remarks refer to the transformations in the binary copper-aluminium alloys described in Dr. Haynes's first two papers, a comparison of which shows the importance of the aluminium content of the alloys on the course of the transformations. The β phase of the hypo-eutectoid alloy appears to transform directly to α and γ_2 , within the temperature range investigated. The β phase of the hypereutectoid alloy transforms directly to α and γ_2 over a narrow temperature range, but at lower temperatures the β first transforms partially

or completely to β_1 . I have examined a hypo-eutectoid binary alloy, using a method similar to that of Dr. Haynes, and the results were intermediate between those obtained by Dr. Haynes on his two alloys. Between 565° and 525° C., pro-eutectoid α separated first, and this gave rise to inhomogeneous β , which then deposited the eutectoid, some of which was lamellar and the remainder cellular. At 525° and 512° C., the pro-eutectoid α was quickly surrounded by an envelope of β_1 . At 500° C. and below, β_1 rosettes formed directly from β ; that is, even in areas remote from pro-eutectoid α . The alloy just described contains 11.3 wt.-% aluminium, a figure obtained both by direct chemical determination and also by measurement of the relative amounts of α and β in equilibrium at 570° C. It appears to me that Dr. Haynes's hypo-eutectoid alloy contained appreciably less aluminium than 11.3 wt.-%, although he gives a figure of 11.4 wt.-%. In other experiments† isothermal transformation of three binary alloys within the composition range 10.4–10.8 wt.-% aluminium resulted in the formation of the β_1 envelope around pro-eutectoid α below 525° C., but no rosette β_1 was detected during transformation down to 450° C.

In his second paper,§ Dr. Haynes gives reasons for regarding β_1 as an ordered form of β . Using four binary alloys within the composition range 11.3–12.4 wt.-% aluminium, I have attempted to determine the metastable β – β_1 phase diagram above 470° C. The results are shown in Fig. A. In constructing the diagram, it has been assumed that metastable equilibrium was established between the two phases within 100 sec., and no allowance was made for any density difference between the two phases. It is interesting to note that the two-phase region seems to disappear at a composition near to that of Cu_3Al . One wonders what form the diagram takes at aluminium contents above this.

Dr. D. R. F. WEST,† B.Sc., D.I.C., A.I.M. (Member): Dr. Haynes, in his second paper,§ gives a value for the $\beta \rightleftharpoons \alpha + \gamma_2$ eutectoid composition in the copper-aluminium system of 11.96 ± 0.05 wt.-% aluminium. This value is slightly higher than that generally accepted. Raynor|| gives 11.80 ± 0.2 wt.-% aluminium, and a recent determination which Mr. Thomas and I have made¶ yielded a value of 11.80 ± 0.15 wt.-% aluminium. This latter determination was made by a method similar to that used by Dr. Haynes, viz. by microscopical measurements of the relative amounts of pro-eutectoid and β phases in samples annealed to equilibrium just above the eutectoid temperature. (Dr. Haynes measured the amount of pro-eutectoid γ_2 in samples transformed just below the eutectoid temperature, but the results of these two investigations should be comparable). For the 12.2 wt.-% aluminium alloy, Dr. Haynes found approximately 6–7 vol.-% γ_2 . One of the alloys which Mr. Thomas and I used contained 12.1 wt.-% aluminium, and the amount of γ_2 was $8\frac{1}{2}$ vol.-%. Thus, there is a slight disagreement between these two sets of results, though this might be due to small inaccuracies in chemical analysis.

Dr. Haynes quotes the accuracy of his determination of the eutectoid composition as ± 0.05 wt.-% aluminium. Does this take into account the possible analytical error? In aluminium bronzes the accuracy of a direct aluminium determination may be taken as ± 0.1 wt.-%. Dr. Haynes determined copper and calculated the aluminium by difference.

* Joint discussion on the following papers published in the *Journal*: R. Haynes, 1953–54, 82, 493; this vol., pp. 105, 357; and R. D. Garwood, this vol., p. 64.

† Metallurgy Department, Imperial College of Science and Technology, London.

‡ D. L. Thomas, D. R. F. West, R. Forscher, and H. F.

Ramstad, *Research*, 1955, 8, (10), S50.

§ R. Haynes, *J. Inst. Metals*, this vol., p. 105.

|| G. V. Raynor, *Inst. Metals: Annotated Equilib. Diagr. Series No. 4*, 1944.

¶ D. L. Thomas and D. R. F. West, *Research*, 1953, 6, (12), S61.

The optimum accuracy of the aluminium figure by this method should again be ± 0.1 wt.-%. The error in measurement of the volume percentage of the γ_2 phase must also be taken into account. Thus, it would appear unjustifiable to claim the limits of accuracy of the eutectoid determination as ± 0.05 wt.-%.

Little information is available concerning the isothermal transformation of aluminium bronzes containing more than approximately 12.3 wt.-% aluminium. Klier and Grymko* have reported on the transformations of a 13.5 wt.-% aluminium alloy, but in view of the marked effect of composition on transformation characteristics, there is need for a knowledge of the course of transformation in alloys containing 12.5–13.5 wt.-% aluminium. Some observations of a preliminary nature have been made at Imperial College on alloys containing approximately 12.5–13.2 wt.-% aluminium. Isothermal transformation at temperatures between approximately 540° and 500° C. resulted in microstructures showing β and β_1 coexisting. However, owing to the rapid separation of appreciable amounts of pro-eutectoid γ_2 , marked compositional gradients were set up in the β matrix, and it is possible that the β and β_1 coexisted because of a depletion of the matrix in aluminium.

Dr. Haynes describes the occurrence of a pink-etching constituent,† containing blue particles, in aluminium bronzes transformed at 350° and 378° C. The pink-etching phase exhibited twinning. He suggests that it may be supersaturated α associated with γ_2 . Recent work‡ has shown the existence of an additional phase in the copper-aluminium system, stable below approximately 350°–400° C. The phase is pink-etching, and has been observed forming from $(\alpha + \gamma_2)$ structures during prolonged annealing treatments at temperatures below approximately 350° C. No twinning was observed. It has been proposed that the phase forms by a peritectoid reaction between the α and γ_2 phases. The phase has also been obtained by the isothermal decomposition of the β phase at 350° C. In both cases additional X-ray-diffraction lines were noted. Thus, the stable pink-etching phase can be formed either as a result of annealing $(\alpha + \gamma_2)$ structures or by isothermal decomposition of the β phase. However, in the latter case it is possible that, in addition to this stable pink-etching phase, there is another pink-etching phase which exhibits twinning and is probably supersaturated α .

Dr. R. HAYNES,§ B.Met., A.I.M. (Junior Member): It was found, by Hickley and Woodhead,|| that the general form of the reaction equation proposed by Johnson and Mehl¶ for transformations proceeding by nucleation and growth:

$$f(t) = 1 - \exp(-Kt^n) \quad (1)$$

where $f(t)$ = fraction transformed, t = time, K and n = constants, did not hold during the later stages of the isothermal precipitation of pro-eutectoid ferrite from austenite in hypo-eutectoid steels. This was attributed to ferrite particles clustering at grain boundaries, which resulted in a much greater impingement effect than was assumed in the derivation of equation (1). To allow for this effect, it was arbitrarily assumed that the rate of transformation was proportional to the square of the fraction untransformed, instead of simply the fraction untransformed, as assumed in equation (1), and the reaction equation:

$$\frac{f(t)}{1 - f(t)} = Kt^n \quad (2)$$

was derived.

An attempt was made to explain equation (2), and for a spherical precipitate the value of $n = 2$ was predicted. Good

agreement was found between experimentally determined values of n for ferrite formation and the predicted value, since the ferrite grew as roughly spherical particles before these impinged on one another.

The precipitation of pro-eutectoid phases in eutectoid copper-aluminium alloys is analogous to the formation of ferrite in steels, and equation (2) should be applicable to these transformations also. Accordingly, the results obtained for the formation of pro-eutectoid constituents in Alloy 2** are shown in Fig. B, where $\log \left(\frac{f(t)}{1 - f(t)} \right)$ has been plotted as

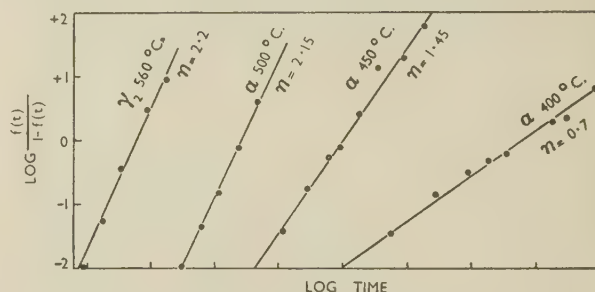


FIG. B.— $\log \frac{f(t)}{1 - f(t)}$ as a Function of Log Time for Pro-Eutectoid Constituents in Alloy 2.

a function of log time. If the reaction equation is followed, the points for a transformation will fall on a straight line whose gradient is n . It is found that in all cases the experimentally determined points lie close to straight lines. The line for the α phase formed at 400° C. is based on an estimation (from data contained in my paper ††) of the amount of α in equilibrium with β (44%), since precipitation of α was prevented from going to completion by eutectoid formation. However, considerable error in this estimation has only a small effect on the value of n . For the γ_2 phase formed at 560° C., the value for n is 2.2; but for the α phase the value of n varies progressively from 2.15 at 500° C. to 0.7 at 400° C.

This variation in the value of n with temperature is probably associated with the fact that the α phase precipitated in two distinct forms: at the grain boundaries and as needles within the grains. At high transformation temperatures (500° C. or higher) pro-eutectoid α occurred mainly as fairly coarse grain-boundary precipitate and as comparatively coarse Widmanstätten precipitate. As the transformation temperature was lowered the α increased considerably in quantity and precipitated mainly as needles, which were the finer the lower the temperature.

In an attempt to explain the observed variation in the value of n with temperature for the α phase, calculations, similar to that of Hickley and Woodhead for precipitation of spherical particles, were made for the precipitation of a phase as thin discs in which growth is edgewise and as rods in which growth is endwise. For these cases the values predicted for n are 1.5 and 1, respectively. Thus, the values of n observed are consistent with the predicted values, within the limits of experimental error, since the form of the precipitate progressively changed from a "blocky" to a fine acicular, i.e. rod-like, form.

The phase γ_2 precipitated randomly throughout the β phase, often as badly formed hexagonal crystals. Such a shape approximates roughly to that of a sphere, and the observed value of n is consistent with that predicted for a sphere.

The value of n predicted for a sphere || is one of the limiting

* E. P. Klier and S. M. Grymko, *Trans. Amer. Inst. Min. Met. Eng.*, 1949, 185, 611.

† R. Haynes, *J. Inst. Metals*, this vol., p. 357.

‡ D. R. F. West and D. Lloyd Thomas, *ibid.*, p. 505

§ Technical Officer, Imperial Chemical Industries, Ltd., Metals Division, Birmingham.

|| C. M. Hickley and J. Woodhead, *J. Iron Steel Inst.*, 1954, 176, 129.

¶ W. A. Johnson and R. F. Mehl, *Trans. Amer. Inst. Min. Met. Eng.*, 1939, 135, 416.

** R. Haynes, *J. Inst. Metals*, this vol., p. 106, Table I.

†† R. Haynes, *ibid.*, p. 110, Fig. 16.

Dr. J. C. CHASTON,* B.Sc., A.R.S.M., A.Inst.P., F.I.M. (Member): It seems to me that some protest is called for against the use in these papers of the term "pro-eutectoid"

It is difficult to understand why Dr. Haynes used an etching reagent which does not reveal martensitic β , while studying reactions below the M_s temperature.[§] The colour changes observed on holding isothermally could be more convincingly interpreted if the initial structure had been re-

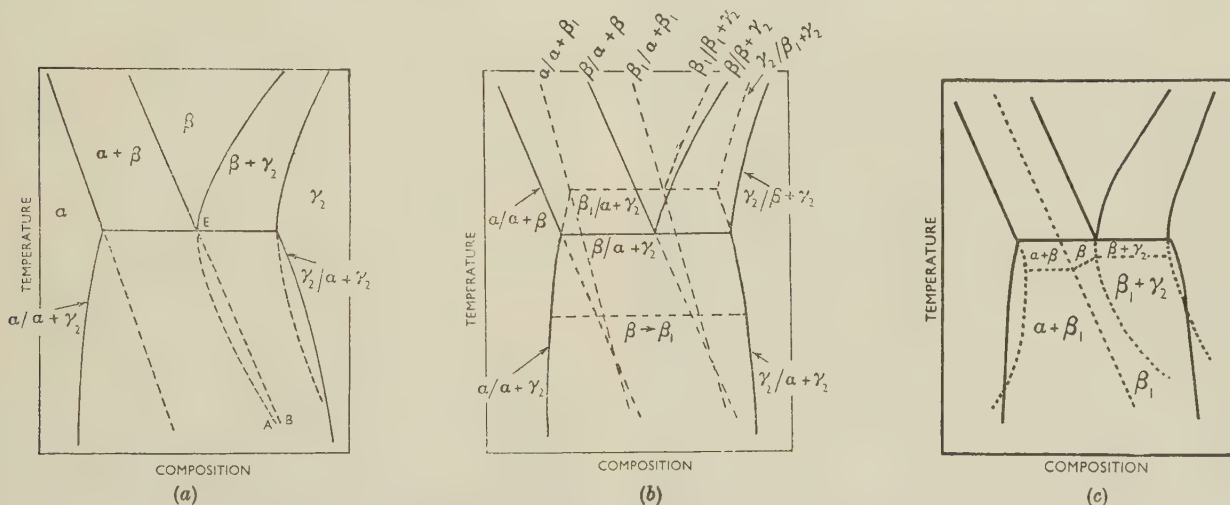


FIG. C.—Hypothetical Phase Diagrams for Copper-Aluminium Alloys. (a) and (b) as proposed by Haynes; (c) as proposed by Miodownik.

The use of the term "pro-eutectoid" has already been criticized by Dr. Chaston. This term was originally used to describe precipitation occurring on cooling to the eutectoid temperature. If the eutectoid nucleates and grows in a pearlitic manner and pro-eutectoid α and eutectoidal α have

Finally, it should be pointed out that Figs. 22 and 23 (reproduced as Fig. C (*a*) and (*b*)) of Dr. Haynes's main paper are thermodynamically incorrect. In Fig. 23 the phase boundaries involving the metastable phase (β_1) must surely be at a *lower* temperature than the boundaries associated with the stable phase (β). The change in direction of the $\beta/(\beta + \gamma)$ boundary in the copper-zinc system is usually attributed to an order-disorder change, and it therefore seems dubious practice to extrapolate the $\beta/(\beta + \gamma)$ boundary in the copper-

|| R. Haynes, *ibid.*, this vol., p. 105.

aluminium system as shown in Fig. 22. It would appear much more logical to assume that the $\beta_1/(\beta_1 + \gamma)$ boundary should be analogous to that in the copper-zinc system. The form of a metastable system does not have to reflect that of the stable system, so that a hypothetical diagram such as Fig. C (c) can be evolved. This diagram is consistent with experimental observations (such as the changes associated with γ precipitation) and is also thermodynamically satisfactory. Such an interpretation might also account for the "massive α " transformation in copper-aluminium alloys being similar to that observed in copper-zinc alloys.*

Mr. J. W. SHEDDEN,† B.Sc., F.I.M. (Member), and Dr. W. I. PUMPHREY,‡ M.Sc. (Member): Our comments are intended not as a criticism of the observations recorded in Dr. Haynes's first paper, but rather as a commentary on their importance in relation to the use of the aluminium bronzes in the form of wire suitable for the production of metal-arc electrodes. In the course of the development of flux-coated electrodes for the metal-arc welding of the aluminium bronzes, we have found it necessary to examine the effect of core-wire composition on the transformation characteristics and mechanical properties of aluminium bronze weld metal, for although the earlier work by Dr. Cook and his co-workers ‡ and the present work by Dr. Haynes provide a reliable guide to the types of structure to be expected in certain aluminium bronzes with various conditions of cooling, the existing data on the isothermal and continuous-cooling transformation characteristics of many of the complex bronzes are far from complete.

There are, of course, a number of aluminium bronzes available for use in cast and wrought form at the present time, but specifications B.S.1400:1948 and B.S.2032/2033:1953 recently issued in an attempt to rationalize the alloy position, relate only to those bronzes containing approximately 10% aluminium with 3% iron, and 10% aluminium with 4% iron and 4% nickel, considered to be typical of those useful to industry. We have found electrodes based on the core-wire alloy containing 10% aluminium with 3% iron most suitable for the general welding of the aluminium bronzes, and core wire of this composition is also covered by A.S.T.M. Specification B.225/48. Such wire can be cut and straightened with the degree of precision necessary for the production of extruded electrodes, and the resulting weld metal is resistant to cracking in multi-run deposits and has attractive mechanical properties. Typical results obtained in tensile tests of specimens machined from blocks of weld metal deposited by electrodes based on the two types of core wire covered by B.S. 2032/2033:1953, are recorded in Table A:

TABLE A.—Tensile Properties of Aluminium Bronze Weld Metals.

Composition of Electrode Core Wire	Weld-Metal Properties		
	0.1% Proof Stress, tons/in. ²	U.T.S., tons/in. ²	Elongation %
10% aluminium, 3% iron	21.0	39.6	18.6
10% aluminium, 4% iron, 4% nickel	31.1	43.8	9.2

It appears to be general practice in this country and abroad for the industrial range of aluminium bronzes to contain a small quantity of iron, largely because of the marked refinement of the high-temperature β phase effected by this addition. It is somewhat disappointing, therefore, that the transformation characteristics of the aluminium bronzes containing deliberate additions of iron have not been studied in some

detail, since iron undoubtedly modifies the transformation behaviour of the aluminium bronzes containing approximately 10% aluminium, with or without additions of nickel.

Dr. Haynes suggests that the precipitation of a large amount of the pro-eutectoid α phase in the aluminium bronzes studied is accompanied by considerable diffusion, and that concentration gradients form within the phases. He suggests, further, that the γ_2 precipitate is nucleated at the interface between the α and β phases, and that it grows by spreading over the surface of the α phase, following in its growth the contour of highest aluminium concentration. On the basis of this suggestion, the γ_2 phase would be expected to segregate, possibly in the form of brittle, intercrystalline films, at the grain boundaries of the original β phase, and such a mode of occurrence of the γ_2 phase could possibly explain the results reported earlier by Rollason and Marsh.§ These workers observed that aluminium bronze weld metal containing, essentially, 93% copper with 7% aluminium, was subject to intercrystalline weakness in multi-layer deposits and suggested that this defect was associated with the presence of

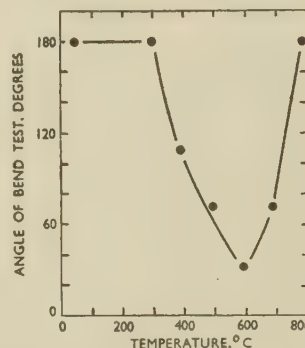


FIG. D.—Results of Hot Bend Tests on Weld-Metal Specimens Containing 93% Copper and 7% Aluminium.

grain-boundary films of a second constituent or some impurity present in the alloy. In later work by the British Non-Ferrous Metals Research Association,|| it was found that multi-layer weld deposits, free from any pronounced susceptibility to intercrystalline weakness, could be produced, if the electrode core wire, and in consequence the deposited weld metal, was of a sufficiently high degree of purity. No trouble was experienced with metal containing 0.0006% bismuth and less than 0.001% lead. Although weld metal of the composition studied by Rollason and Marsh theoretically consists wholly of α phase, it is likely, in practice, to contain cored regions relatively high in aluminium, and in consequence some β phase may be present and is likely to be located at the grain boundaries. Any subsequent eutectoid transformation could conceivably result in the formation of the γ_2 phase at the crystal boundaries, with consequent embrittlement of the metal. It is of interest to note that weld metal of the composition examined by Rollason and Marsh exhibited intergranular weakness only in multi-layer deposits, where the reheating of any one layer of solid weld metal by the deposition of subsequent layers may possibly be conducive to the occurrence of the eutectoid transformation at the grain boundaries.

The results of hot bend tests on specimens of weld metal of the composition studied by Rollason and Marsh are shown in Fig. D; the existence of a second constituent at the grain boundaries of a specimen of this weld metal, water-quenched from 600°C. after being maintained at that temperature for 30 min. is illustrated in Fig. E (Plate LXXX).

The brittleness which occurs in multi-layer deposits of aluminium bronze weld metal containing 7% aluminium, may

* D. Hull and R. D. Garwood, *Symposium on the Mechanism of Phase Transformations in Metals (Inst. Metals)*, 1955, 219.

† Murex Welding Processes, Ltd., Waltham Cross, Herts.

‡ M. Cook, W. P. Fentiman, and E. Davies, *J. Inst. Metals*, 1951-52, 80, 419.

§ E. C. Rollason and W. D. Marsh, *Welding*, 1947, 15, 252.

|| E. C. Mantle, *Engineering*, 1951, 172, 443.

be overcome by increasing the aluminium and iron content of the deposited weld metal, with the resultant formation of a duplex structure of fine grain-size, possibly because in such a structure the brittle γ_2 phase does not form preferentially at the grain boundaries.

Dr. R. HAYNES (*in reply*): Commenting on the difference between the transformation of my hypo-eutectoid Alloy 0 and of another alloy of apparently the same composition, Mr. Thomas suggests that the analysis of my alloy may be in error. Estimates made on a few photomicrographs of a specimen of Alloy 0 transformed at 560° C. indicate that there is about 50% pro-eutectoid α , which corresponds to about 10.7% aluminium. In view of this discrepancy between the compositions as determined by chemical analysis and by quantitative metallography, a small specimen was submitted for an independent chemical analysis and the aluminium content reported is $10.8 \pm 0.1\%$ (mean of two determinations made by different direct methods). This value for aluminium content is consistent with Mr. Thomas's observations. The remaining alloys subsequently have been checked in a similar manner for aluminium content and satisfactory agreement found between the values quoted in the papers and the new analyses. Dr. West points out that the accuracy of the estimation of the eutectoid composition is unlikely to be as high as is claimed in the paper, and this is borne out by the recent analysis. Thus, it now appears that the error is not greater than $\pm 0.2\%$. The original estimate was based upon the original analyses, all of which were within $\pm 0.05\%$ of the mean value.

Mr. Thomas's phase diagram relating to the β and β_1 phases is interesting and is of the form suggested in my second paper. The steep slope of the $(\beta + \beta_1)/\beta_1$ phase boundary suggests that β_1 may be able to exist only over a narrow range close to the composition Cu_3Al and that β_1 is based on this composition.

Dr. Chaston and Dr. Miodownik criticize the use of the term "pro-eutectoid". Apparently the choice lies between two words: "primary", derived from Latin, meaning "first in order of time or development", and "pro-eutectoid", derived from Greek, meaning "before the eutectoid", both of which adequately describe the constituent. The latter is used extensively in ferrous metallurgy and in titanium metallurgy,* and it seems to me that it is preferable to use the term that has already gained acceptance in these other fields of metallurgy. Despite Dr. Miodownik's assertion to the contrary, the pro-eutectoid phase can be distinguished easily from the eutectoid and, in these alloys, the adjective "pro-eutectoid" precisely describes the constituent. The distinguishing feature of a pro-eutectoid constituent is that it is formed before the eutectoid, and whether it has the same orientation as the same phase in the eutectoid or not is immaterial.

The term "eutectoid" is generally used to describe the product when a single solid phase decomposes to form, in the case of a binary alloy, two new solid phases. On this definition the structures described in the papers may legitimately be described as eutectoid. To differentiate between the various forms of decomposition products would lead to considerable confusion in terminology.

Two etching reagents were employed in the study of reactions below the M_s temperature, one of which reveals martensitic β . Examination of the phases formed isothermally below the M_s temperature is facilitated by the use of a reagent which does not reveal the martensite formed on subsequent quenching, because such martensite tends to obscure the products of isothermal reactions. However, this does not imply that no specimens were examined after etching in the reagent which reveals martensite. It became clear early in the investigation that there was no advantage in using the reagent which reveals martensite, and hence most of the work was done on specimens etched in the other reagent.

Dr. Miodownik comments on the resemblance between Fig. 8 (Plate XLVIII) of my paper and Fig. 4 (Plate XII) of Mr. Garwood's paper. A much closer analogy exists between the α formed in approximately eutectoid copper-aluminium alloys at 425° and 400° C. and that illustrated in Fig. 4 of Mr. Garwood's paper. This α is quite distinct in appearance from the products of transformation formed below the M_s temperature, and leads me to believe that the mechanism of decomposition below the M_s temperature is not bainitic.

Dr. Miodownik is in error when he states that Figs. 22 and 23 in my second paper are thermodynamically incorrect. The phases α , β , and γ_2 only are referred to in Fig. 22 (reproduced as Fig. C (a)), and the diagram is consistent both with the data and with thermodynamic principles. No suggestion is made, or intended, about the form of the $\beta_1/(\beta_1 + \gamma_2)$ phase boundary. In connection with the change in the direction of the $\beta/(\beta + \gamma_2)$ phase boundary, it should be pointed out that the interpretation of the data that has been adopted is simpler than the assumption of an order-disorder change. Moreover, there is much evidence to suggest, although not conclusively, that β_1 is the ordered form of β and the change in the direction of the phase boundary occurs at a temperature above that at which β_1 is first observed.

Fig. 23 (reproduced as Fig. C (b)) shows the probable relationship between the phases α , β and β_1 , with reference to the stable equilibrium diagram, in a simplified form. The relationship between β and β_1 , which is of the form shown in Mr. Thomas's diagram, has been omitted, the critical temperature at which β_1 forms from β simply being indicated by a horizontal line. It can be demonstrated, by thermodynamics, that above the critical temperature the hypothetical phase boundaries for α in equilibrium with β_1 and β_1 in equilibrium with α should be higher than the analogous phase boundaries for α in equilibrium with β and β in equilibrium with α , and that below the critical temperature the phase boundaries relating to β_1 should be lower than those relating to β . The $\alpha/(\alpha + \beta)$ and $\alpha/(\alpha + \beta_1)$ phase boundaries cross a little below the critical temperature, whilst the $\beta/(\alpha + \beta)$ and $\beta_1/(\alpha + \beta_1)$ phase boundaries cross a little above the critical temperature (the intersection of these latter phase boundaries is shown erroneously below the critical temperature in Fig. 23). The hypothetical diagram, Fig. C (c), suggested by Dr. Miodownik is both incorrect thermodynamically and is inconsistent with the experimental data, for the diagram indicates that below the temperature at which β_1 forms, a region exists in which β_1 has a stable existence, similar to β in the copper-zinc system.

It is interesting to learn of the relevance of my earlier paper to the welding of aluminium bronzes. Further studies of transformations of hypo-eutectoid aluminium bronzes, especially the more complex ones, would be valuable; unfortunately, time did not permit extension of the investigation described. Nickel additions were chosen in preference to additions of iron because complications introduced by a fourth phase were avoided.

Occurrence of intergranular weakness in multi-layer weld deposits, where reheating of layers of solid weld metal is caused by the deposition of subsequent layers, may be due to formation of γ_2 . It has been observed that, at the same temperature, reheated β_1 decomposes into $(\alpha + \gamma_2)$ much more rapidly than β isothermally transforms to $(\alpha + \gamma_2)$.

I am indebted to the Research Department, Metals Division, Imperial Chemical Industries, Ltd., Birmingham, for carrying out the chemical analyses.

Mr. R. D. GARWOOD (*in reply*): Both Mr. Lloyd Thomas and Dr. Miodownik have drawn attention to the similarity between the structures developed during the early stages of transformation at low temperatures in copper-zinc and copper-aluminium alloys. A careful inspection of the photomicrographs in the papers by Smith and Lindlie† and by Mack‡ on the transformations in copper-aluminium alloys

* F. C. Holden and R. I. Jaffee, *Titanium Met. Lab. (Battelle Mem. Inst.) Rep.*, 1955, (25), p. 36.

† C. S. Smith and W. E. Lindlie, *Trans. Amer. Inst. Min. Met. Eng.*, 1933, 104, 69.

‡ D. J. Mack, *ibid.*, 1948 175, 240.

of eutectoid composition, will show that there is a distinct change in the appearance of the α constituent between 500° and 475° C. The rather irregular particles precipitated at the higher temperatures are replaced by the V-shaped formations characteristic of the bainite reaction in brass. Similar structures occur during the isothermal transformation of the eutectoid alloy in the silver-cadmium system at 200° C.* Indeed, there is no reason why a bainite reaction should not be found in any alloy which undergoes a martensite transformation, provided that the two conditions mentioned in my paper are satisfied.

The mathematical analysis of the isothermal reaction curves carried out by Dr. Haynes has some bearing on the mode of growth of the α phase in copper-aluminium alloys. The decrease in the value of the coefficient n between 560° and 400° C. in Alloy 2 has been attributed to a gradual change from a "blocky" to an acicular or rod-like form of precipitate. On this point I must disagree with Dr. Haynes and am of the opinion that direct microscopical observation is more reliable than an analysis using a rate equation based on arbitrary assumptions. If the behaviour in the two systems, copper-zinc and copper-aluminium, is analogous, then two modes of decomposition can occur simultaneously within a narrow temperature range. At high temperatures the "blocky"

particles develop with a non-coherent interface, but at lower temperatures, i.e. below 500° C., in the copper-aluminium alloy of eutectoid composition, decomposition proceeds coherently by the growth of thin plates—not needles. The type of coherency envisaged is that which exists at a martensite interface and will give rise to surface-relief effects. The plates invariably occur in pairs, producing the characteristic V-shaped formation in the polished surface, and form parallel to crystallographic planes of the type $(1kk)_\beta$ and $(\bar{1}kk)_\beta$. This is an example of co-operative nucleation, for both plates appear to grow from a line source parallel to the $[0\bar{1}1]_\beta$ direction which is common to the two planes.

This type of growth is illustrated in Fig. F (Plate LXXX), which represents a 58.7% copper, 41.3% zinc alloy transformed isothermally at 205° C. for 93 hr. Two particles are visible in which the plates lie approximately parallel to the polished surface. It will be seen that the precipitate adopts the form of a paper dart, with growth taking place most rapidly parallel to the common direction. Since the publication of my paper, I have established that the habit planes adopted by the bainite plates do not alter as the transformation temperature is raised to 360° C., the highest temperature at which the V-shaped formations were observed in brass.

Discussion

Equilibrium Relations at 460° C. in Aluminium-Rich Alloys Containing 0-7% Copper, 0-7% Magnesium, and 2.0% [0.6%, and 1.2%] Silicon

By H. J. AXON

(*Journal*, 1952-53, 81, 209, 449, and this vol., p. 490)

Mr. D. L. W. COLLINS,† B.Sc. A.R.S.M. (Member): Dr. Axon has indicated in the title and text of his papers that he was investigating equilibrium relations, and it is indeed probable that after four weeks' annealing the alloys examined were very close to equilibrium. The results of such an investigation are potentially of considerable value both academically and industrially, and it is unfortunate that in their interpretation he has ignored some of the geometrical corollaries of the phase rule, and thus produced a picture of the 460° C. isotherm of the quaternary system which is in some aspects impossible under equilibrium conditions and in others highly improbable. This oversight is the more unfortunate in that it is possible to produce diagrams which are consistent within the limits of experimental error with the reported results, but in which the anomalies are removed, as in Figs. A and B.

One of the implications of the phase rule is that any four-phase region in a quaternary isothermal is bounded by a tetrahedron, the six edges of which join the phases in pairs, so that any two parallel sections of such a region should be exactly similar geometrically (rather than of "approximately similar dimensions" which Dr. Axon remarks on as being an interesting property of the $(\alpha + \text{Mg}_2\text{Si} + \theta + S)$ field) and should have the same orientation with respect to the axes. Thus, to take one example, the boundaries of the $(\alpha + \text{Si} + \theta + Q)$ and $(\alpha + \text{Mg}_2\text{Si} + \theta + Q)$ fields which mark the appearance of θ (e.g. NO and PT in Fig. A) should be exactly parallel in a section at any one silicon level; this is patently not true of the sections as drawn by Dr. Axon, which therefore cannot possibly represent equilibrium relations in all three diagrams.

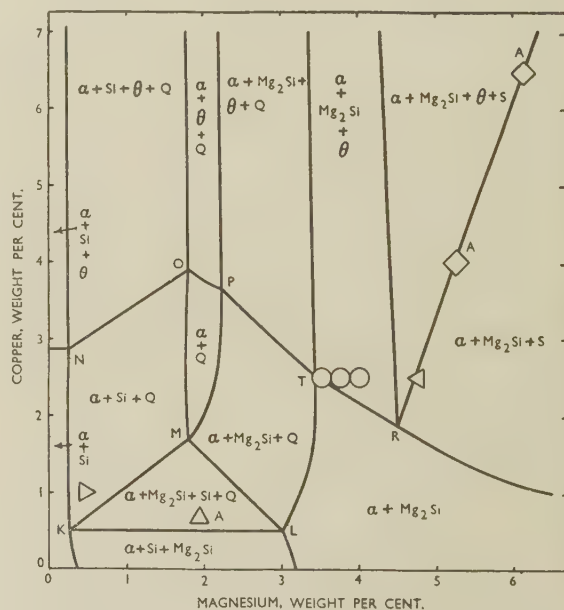


Fig. A.—Section of the 460° C. Isothermal for the System Aluminium-Copper-Magnesium-Silicon at 2.0% Silicon.

* G. R. Speich and D. J. Mack, *Trans. Amer. Inst. Min. Met. Eng.*, 1953, 197, 549.

† Aluminium Laboratories Limited, Banbury.

While the fourth quaternary region, the $(\alpha + \text{Mg}_2\text{Si} + \text{Si} + Q)$ field, is as shown theoretically possible, its shape and position are nevertheless highly improbable; the points designated K and L in Fig. A are sections of the edges of the tetrahedron which join the point G in the α field (Fig. 2, p. 491 of the third paper) to Si and Mg_2Si , respectively, and the slopes of these edges which are indicated by Dr. Axon's sections at 1.2 and 2.0% silicon imply that both the Si and Mg_2Si phases in equilibrium with α and Q dissolve about 40% copper, and the Si phase dissolves about 25% magnesium in addition! The third edge of the tetrahedron, which is represented by the apices of the triangular sections (M in Fig. A), joins the point G in the α field to the Q phase, but the possible compositions of Q indicated by the slope of this line are greatly different from that obtained by chemical analysis by Phragmén,* which is quoted in the papers. This again is quite possible if a wide composition range is assumed for the Q phase, but it is made improbable by the fact that the α phase in equilibrium with Phragmén's Q must have a composition in which the relative contents of magnesium, silicon, and copper are very similar to those at the point G , as may be deduced from the compositions of Q and the alloy from which it was extracted.

These anomalies may be removed by redrawing the sections of the phase field as in Figs. A and B, which involves moving

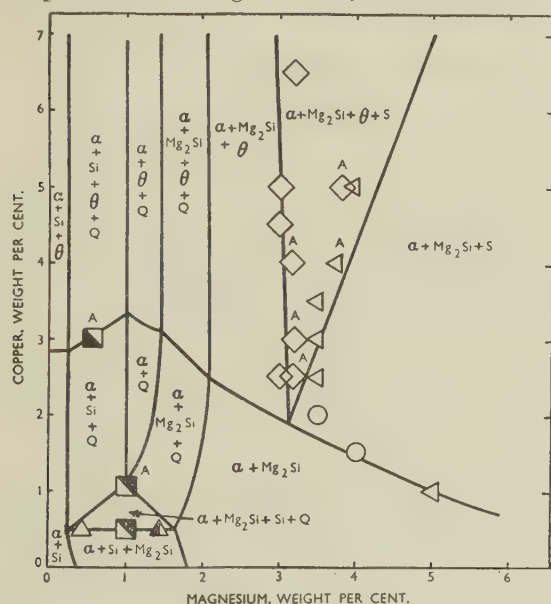


FIG. B.—Section of the 460° C. Isothermal at 1.2% Silicon.

the line KL in the 2.0% silicon section to the same copper level as in the 1.2% section, and slightly altering the slopes of the lines KM and LM and their equivalents in the 1.2% section. This arrangement has the added advantage of placing the alloy containing Si 2.0, Cu 1.0, Mg 0.5%, which is reported to contain α , Si, and Q , in the $(\alpha + \text{Si} + Q)$ field, thus compensating for the inclusion of the alloy containing Si 2.0, Cu 0.7, Mg 1.9% in the quaternary field. With regard to the latter alloy, on which the position of the line equivalent to KL in Dr. Axon's diagram (Fig. 1, p. 491) appears to have been based, there is a possibility of experimental error which may have arisen in one of three ways: first, since no analysis was made for copper, this element may have been at a lower level than was believed; secondly, the Q phase may actually have been present in the alloy without being observed in the particular sections examined; or thirdly, the alloy may not have attained a near-equilibrium condition at 460° C.

It may be noted that the alteration of the slopes of the lines KM and LM to conform with the analysed composition of Q brings them substantially parallel with the lines NO and PT , respectively; this is to be expected in the absence of very wide

composition ranges in the phases concerned, since each of the lines KM and NO is a section of a plane joining a point in the α field to Si and Q , and LM and PT are sections of planes connecting α with Mg_2Si and Q .

As has been implied earlier, it is extremely unlikely that an ionic compound such as Mg_2Si will exist over a range differing appreciably from its stoichiometric composition, so that lines joining this phase with points on the α field will be almost parallel with each other and with the aluminium-magnesium-silicon plane. The three points in a section at constant silicon which represent such lines (L , T , and R in Fig. A) will thus retain almost identical relative positions from one low-silicon level to another, and the copper content of each will not appreciably alter; that is, the imaginary triangle with L , T , and R as its apices should have the same shape, size, and orientation in the 1.2% silicon section as in the 2.0% section, and should be translated in a horizontal direction only. Adjustment of the diagrams to produce this result places two alloys (Si 2.0, Cu 2.5, Mg 4.0% and Si 2.0, Cu 2.5, Mg 3.75%) on the wrong side of the boundary marking the limit of occurrence of θ , but this appears to be permissible since they are unanalysed alloys, the classification of which depends on the presence or absence of a very small quantity of θ , which may have been present but unobserved.

The necessity for the positioning of the point R which leads to the "misplacing" of these two alloys arises from consideration of the $(\alpha + \text{Mg}_2\text{Si} + \theta + S)$ field, the sections of which must, as has been said, be geometrically similar, and will almost certainly be nearly identical in shape with the $(\alpha + \theta + S)$ field in the ternary system aluminium-magnesium-copper. In order to satisfy these conditions, and to include as many as possible of the analysed alloys in their appropriate fields, the position of the quaternary field must be substantially as shown in Figs. A and B; a number of alloys at the 1.2% silicon level now appear in the wrong field, but, from the error in magnesium content found in all the analysed alloys, this is probably due mainly to errors in the composition. There does, however, appear to be more doubt about the equilibrium position of this field than in other cases, particularly in respect of the boundary with the $(\alpha + \text{Mg}_2\text{Si} + S)$ field; extrapolation to the 0.6% silicon level from the sections in Figs. A and B gives a perfect fit with the reported results in all other phase fields at this silicon content, but two analysed alloys reported to contain only α , Mg_2Si , and S are placed in the $(\alpha + \text{Mg}_2\text{Si} + \theta + S)$ field.

Extrapolation of the four-phase fields in the amended diagrams in Figs. A and B to their points of disappearance produces the model of the α field shown in Fig. C, which, as would be expected, has the same general form as that given by Dr. Axon, though it differs considerably in detail, the most notable variation being in the position of the point D which no longer requires the solubility of silicon in α containing 1.2% magnes-

	Cu, %	Mg, %	Si, %
A	2.85	0.00	0.50
B	2.85	0.25	0.40
C	2.50	0.45	0.25
D	1.95	1.20	0.02
E	2.90	0.00	0.00
F	2.75	1.20	0.00
G	0.50	0.25	0.40
H	0.00	0.35	0.35
J	0.00	0.00	0.51

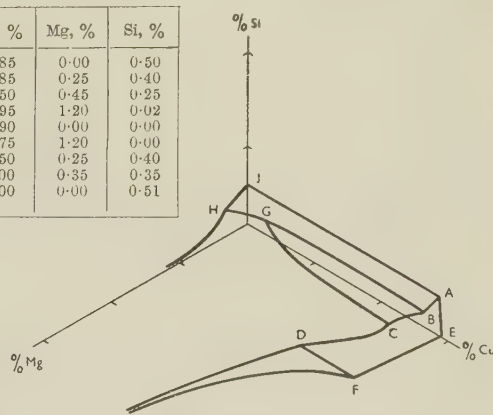


FIG. C.—The Form of the Aluminium-Rich α Solid Solution in the System Aluminium-Copper-Magnesium-Silicon at 460° C.

* G. Phragmén, *J. Inst. Metals*, 1950, 77, 489.

ium to increase with increasing copper. It is not claimed for these three diagrams that they represent exactly the 460° C. isotherm of the aluminium-magnesium-silicon-copper system, but it is believed that on Dr. Axon's data they are a closer approximation to equilibrium relations than those presented by the author himself, and it is hoped that, with this discussion, they will indicate the regions which need further checking in order to arrive at a yet closer approximation.

The AUTHOR (*in reply*): Whilst the majority of alloys were analysed for magnesium only, a proportion were analysed also for copper and/or silicon. This was done partly as a general check on the accuracy with which synthetic compositions were attained in practice, and partly as a further check on alloys the microstructures of which did not appear to be in harmony with their synthetic compositions. In particular, the alloy which Mr. Collins designates (Si 2.0, Cu 0.7, Mg 1.9%) was analysed for both magnesium and copper; the reported analyses being 0.72% copper; 1.89 magnesium. The two

analysed alloys in the stick immediately above this were also analysed for copper and were found to contain 0.92 and 0.99% copper, respectively. This fixes the position of the line *KL* between 0.72 and 0.92% copper.

Thus, Mr. Collins's most interesting modifications to the ($\alpha + \text{Mg}_2\text{Si} + \text{Si} + Q$) phase field may well be justifiable in terms of theoretical equilibrium, but they are not in accord with the experimental observations obtained in the present work.

Furthermore, the modifications which Mr. Collins has felt impelled to make to the ($\alpha + \text{Mg}_2\text{Si} + \theta + S$) phase field require that too many of the experimental observations be discarded. Now it may be argued that the diagrams as presented do not represent equilibrium conditions, but at least they do summarize the results of the experiments. It is difficult to say what significance should be attached to modifications of the experimental diagrams which are obtained by discarding results from the most carefully examined alloys.

Discussion

Specific-Heat Measurements on Aluminium-4% Copper and Aluminium-4% Copper-Tin Alloys

By I. J. POLMEAR and H. K. HARDY

(*Journal*, this vol., p. 393)

MR. K. HIRANO*: Mr. Polmear and Dr. Hardy have carried out specific-heat measurements on aluminium-4% copper and aluminium-4% copper-tin alloys and have confirmed the very great acceleration of the precipitation process caused by the addition of tin. It may be noted that similar work has been undertaken by Japanese investigators. Morinaga, Yamada, and Takahashi† have obtained instantaneous specific-heat/temperature curves for aluminium-4% copper-0.1% tin alloys. Their results are in qualitative agreement with those of the British workers.

In relation to the study of the precipitation rate by means of specific-heat measurements, it may be worth while to cite some unpublished work of my own. To examine the effect of grain boundaries on the precipitation rate, I made specific-heat measurements on polycrystalline and single-crystal specimens of aluminium-4% copper alloy of very high purity, employing the method developed by Nagasaki and Takagi.‡ The rate of heating was 2°–3° C./min. The temperatures observed, which define the specific-heat/temperature curves, are given in Table A.

TABLE A

Al-4% Cu Alloy.	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
	Temperature, °C.				
Single-crystal (water-quenched from 540° C.)	214	235	315	354	420
Polycrystalline (water-quenched from 540° C.)	216	220	285	327	420

For *b*, *c*, *d*, *e*, *f*, see Fig. 1 (p. 393) of the paper by Polmear and Hardy.

The heat evolved on precipitation (area *cde*) was about 4.2 cal./g. for both specimens, being unaffected by the presence

or absence of grain boundaries. The fact that the temperature, *d*, at which the maximum rate of heat evolution due to precipitation of θ' occurs, was 315° C. in the single-crystal, as compared with 285° C. in the polycrystalline specimen, illustrates the retardation of the precipitation process caused by the absence of grain boundaries.

I have also carried out specific-heat measurements on aluminium-30% silver and aluminium-30% silver-0.5% tin alloys.§ As opposed to the aluminium-copper alloys, a slight shift of the temperature of *d* to higher values (from 270° to 282° C.) due to the addition of tin, has been recorded.

Thus, it is apparent that a small quantity of added tin does not necessarily accelerate the precipitation process in alloys.

Although the view that tin facilitates the nucleation process may explain the enhanced rate of θ' formation in aluminium-copper alloy, it would seem that the influence of tin on the grain-size cannot be neglected in elucidating the part which it plays. Microscopic observations might supply useful information on this point.

The AUTHORS (*in reply*): We are interested to note that Mr. Hirano has found a difference in the temperatures at which single-crystal and polycrystalline specimens of aluminium-4% copper alloy show their maximum rate of precipitation of θ' on heating. The deduction that this temperature was lower for the polycrystalline specimen because the grain boundaries accelerated the precipitation appears to be correct, provided that each specimen had received effectively the same amount of cold work during or after quenching. All our specimens were polycrystalline, although those containing tin had a grain-size somewhat finer than those of the tin-free alloys. However, we are quite certain that this would have only an insignificant influence on the effects which we have attributed to tin.

It is interesting to note that tin does not accelerate precipitation in aluminium-30% silver alloy.

* Department of Physics, Tokyo Institute of Technology, Tokyo, Japan.

† T. Morinaga, M. Yamada, and T. Takahashi, *Nippon Kinzoku Gakkai-Si*, 1954, 18, 350.

‡ S. Nagasaki and Y. Takagi, *J. Appl. Physics Japan*, 1948, 17, 104.

§ To be published in *J. Phys. Soc. Japan*.

Discussion

Mechanical Twinning in Molybdenum

By R. W. CAHN

(Journal, this vol., p. 493)

Dr. G. A. ALERS*: In the discussion and summary of his paper, Dr. Cahn concludes that the ductile-to-brittle transition is a characteristic of polycrystalline material, since he observes considerable ductility in single crystals in a compression test. Although we agree with this conclusion, we would like to point out that ductility of brittle materials is to be expected in a compression test. The brittle fracture of a specimen is caused by the rapid propagation of a crack through the material, since this is the only way two planes of atoms can be separated at the stress levels usually involved. A crack cannot propagate by itself, unless there is a tensile stress to pull it open. In a compression test, there are no tensile stresses until some plastic deformation has occurred. Thus we should anticipate no brittle fracture until the specimen has been deformed enough to create a sufficient tensile stress to allow propagation of a crack.

On the basis of this argument, we have conducted compression tests on polycrystalline molybdenum down to -196°C . and have found the material quite ductile. In all cases the test was stopped after a reduction in height of 20%. Metallographic examination of the specimens tested at -196° and -100°C . showed many small grain-boundary cracks near the centre line of the cylindrical specimens. These cracks seemed to run parallel to this centre line (which was in the direction of the applied compressive stress) and at right angles to the direction of the tensile stresses developed by the barrelling out of the specimen during plastic deformation. In agreement with Cahn, we observed no appreciable twinning at the relatively low strain rate of 100%/hr. which we used.

The fact that all the microcracks which were formed during a 20% reduction in height at -196°C . appeared in the grain boundaries is very interesting. If this same material were tested in tension, a brittle fracture would have occurred after less than 0.01% plastic flow, and the fracture surface would have been of a cleavage type. This means that the crack propagates mostly by cleavage, even though it is nucleated by grain-boundary failure. This conclusion has also been reached by careful examination of the fracture surface of tensile specimens, as well as the examination of the tension side of bend specimens. It is therefore important to realize that the fracture surface is characteristic of the path chosen by a rapidly growing crack and does not necessarily imply anything about the origin of the fracture.

The AUTHOR (*in reply*): While it is not unexpected for polycrystalline material to have some capacity for deformation in compression (I hesitate to use the term "ductility" for a compressive test!), it is certainly surprising that a deformation as great as 20% reduction in height can be imparted at a temperature at which tensile ductility is nil. Dr. Alers' experiments are eloquent proof that the nucleation and the spread of a fracture are determined by quite distinct influences. The special feature of those of my single crystals which did not twin was that no crack was nucleated; hence their exceptional compressibility.

I note that the compression was very slow. Would the polycrystalline specimens still be so highly compressible if they were tested in impact at low temperatures?

Discussion

The Constitution of Uranium Alloys †

Mr. BROOK and Dr. WILLIAMS (*in reply*): In the Laves phases, AB_2 , the ratio of the interatomic distances of like atoms, d_{AA}/d_{BB} must of necessity be 1.225 in the $C15$ structure and close to this in the $C14$ and $C36$ structures. Whether this phase forms or not will depend, not only on the ratio of the interatomic distances in the pure metals, d_A/d_B , but also on the extent to which the interatomic distance of one element can be compressed or expanded in relation to that of the other. In fact, the ratios d_A/d_B differing markedly from the ideal 1.225, which Dr. Hume-Rothery finds unconvincing, frequently correspond to compounds of metals one of which has a particularly high compressibility, such as the alkali and alkaline earth metals, &c. (Other abnormal ratios include compounds of manganese; in this case there is some doubt as to what interatomic distances should be taken for pure manganese.)

We are most interested in Dr. Hume-Rothery's suggestion that the real cause of the formation of Laves phases may lie in the tendency for the larger A atoms to form tetrahedral bonds between themselves. As there are Laves phases with A atoms from practically all groups of the Periodic Table, Dr. Hume-Rothery's suggestion is tantamount to saying that most metallic atoms tend to form tetrahedral bonds between themselves, provided that there are present atoms small enough to

fill the necessary spaces to stabilize the structure. Hence the factor determining the structure is not so much the tendency to tetrahedral bonding as the size of the smaller atoms in relation to the larger. For example, chromium and manganese form the Laves phases CrBe_2 and MnBe_2 with the smaller beryllium, and ZrCr_2 and ZrMn_2 with the larger zirconium atoms. Similarly, sodium forms KNa_2 and NaAu_2 , and magnesium CaMg_2 and MgCu_2 .

We wonder if the fact that there are more examples of Laves phases in which the A element is taken from Group IVa, e.g. titanium and zirconium, may arise because there happens to be a large number of elements of convenient size to act as B atoms, rather than that Group IVa elements have a greater tendency for tetrahedral bonding. For example, the three Long Periods each contain several transition metals of similar atomic size, i.e. vanadium-nickel, molybdenum-palladium, and tungsten-platinum. The first group has the correct size to be capable of forming Laves phases with titanium and all three with zirconium and most of the possible phases are known to exist. Similarly, most of these transition metals take the part of the A element in forming Laves phases with the only convenient B element, beryllium.‡ Thus, the Group IV elements show no greater tendency to form these structures

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† For discussion, see *Journal*, this vol., pp. 535-540.

‡ Nickel is exceptional in that, although of suitable size, it does not form Laves phases with titanium, zirconium, or beryllium.

with the conveniently sized transitional metals than do the latter with beryllium.

We agree with Dr. Waldron that a comparison of the Laves phases of uranium and transition metals with those of other systems does not allow deduction of apparent valency numbers of any real significance.

As we stated in our paper, the ratios d_G/d_M are consistent with Berry and Raynor's general observation that the C14 structure is formed at or near the ideal ratio of 1.225, with the C15 replacing it at higher and lower ratios. Thus in Table

V (p. 275), as the ratio decreased from 1.241 for UNi₂ (C14), the C15 structure occurred at 1.236 (UCo₂) and lower ratios. The fact that the C15 structure occurred at the ideal ratio in this series is not of great significance, particularly as a case could be made for other values for the interatomic distances of uranium, &c., in Table V, which would alter relative ratios rather than change the order. The important point, as Dr. Waldron has pointed out, is that the ratio for UNi₂ should lie at one end of the range for the C15 structures, and that this should be at the end nearer the ideal ratio.

Discussion

Plastic Deformation of Aluminium-3.5% Copper Alloy Single Crystals

By K. M. CARLSEN and R. W. K. HONEYCOMBE

(*Journal*, this vol., p. 449)

Mr. N. A. MCKINNON,* M.Sc. (Member): The air-cooled single crystals of aluminium-3.5% copper alloy investigated by Mr. Carlsen and Professor Honeycombe, deformed on a single slip system and overshoot the [100]-[111] boundary in a similar way to single crystals of 70:30 α -brass. It has been suggested by Cottrell† that the behaviour of α -brass is due to short-range order. The initial dislocations to move have to disrupt the short-range order, so that the stress needed to keep the dislocation sources operating falls slowly until the order on the slip planes is destroyed. A large elongation with a low rate of strain-hardening may then be expected on the primary system until the conjugate system has slipped sufficiently for the "softening by disordering" process to occur. Overshoot of the [100]-[111] boundary would thus be observed.

While it is unlikely that the amount of short-range order expected in a concentrated solid solution like 70:30 α -brass would be found in an aluminium-3.5% copper solid solution, this could be increased greatly in the event of preprecipitation during air-cooling. That this is likely is suggested by my study of the effect of various rates of quenching on the hardness and metallographic structure of an aluminium-3.8% silver alloy. Specimens only slightly larger than those of Carlsen and Honeycombe, which thus would have experienced approximately the same rate of cooling, had a hardness of 35.6 V.P.N. compared with 22.0 for specimens given the optimum quench for this alloy. This consists of cooling from 610° to 410° C. in 3 min., followed by a quench into boiling water with final cooling in cold water. After such a quench and appropriate ageing treatment, there has been no evidence of any preferential precipitation. The difference in hardness values is such that even allowing for variations in the rate of age-hardening of the two alloy systems, it would seem that Carlsen and Honeycombe's air-cooled crystals were in a partly aged condition before deformation and thus would give short-range order effects.

My interest in studying the deformation of quenched single crystals has been in "middle" orientations at low elongations, for which only the expected single-slip system was observed on the surface in all cases. However, after a deformation of 2%, one crystal, oriented near the [100]-[111] boundary, showed

slip traces of the primary, conjugate, and cross-slip systems, indicating that there was no overshoot of the boundary. Stress/strain curves have been determined for only a few crystals up to 5% elongation, so that no conclusion can yet be reached on the comparative behaviour of quenched and air-cooled crystals.

A further point arises from a consideration of the rate of work-hardening of Carlsen and Honeycombe's crystals. On deforming at -196° C., where the effects of ageing during deformation are avoided, the increase in applied shear stress was about 7.5 kg./mm.² for a glide strain of 1. This may be compared with a figure of 6 kg./mm.² for deformation at room temperature of crystals of similar orientation of high-purity aluminium.‡ It would seem that the rate of work-hardening is relatively independent of the yield stress, which affords further evidence of an effect of order in determining the yield stress of solid solutions.

The AUTHORS (*in reply*): We agree that the air-cooling of our crystals might have been insufficiently rapid to prevent partial ageing, in which case some clustering of solute atoms would have occurred. Unfortunately, there are no data on the relative hardness of the water-quenched and air-cooled crystals used in our experiments, which could confirm this suspicion. Short-range order may well influence the amount of overshoot in this type of alloy, but the phenomenon is also encountered in alloys which would not be expected to exhibit much short-range order. For example, recent unpublished work by Greetham and Honeycombe has shown that single crystals of aluminium- $\frac{1}{2}$ % silver alloy overshoot the [100]-[111] boundary, although this alloy is a solid solution at room temperature and partial ageing cannot take place.

The rate of work-hardening appears to be independent of the yield point in fully aged alloys (Fig. 16, p. 453 of our paper). However, it seems doubtful whether the comparison made by Mr. McKinnon between the work-hardening of an air-cooled 3.5% copper alloy crystal deformed at -196° C. and an aluminium crystal deformed at room temperature is good evidence for the effect of order on the yield stress of solid solutions.

* Department of Supply Laboratories, Melbourne, Australia.

† A. H. Cottrell, *Relation of Properties to Microstructure*

(*Amer. Soc. Metals*), 1954, 131.

‡ H. Lange and K. Lucke, *Z. Metallkunde*, 1953, 44, 183.

Discussion

The Selective Oxidation of Nickel-Chromium Alloys at High Temperatures

By J. MOREAU and PROFESSOR J. BÉNARD

(Journal, this vol., p. 87)

Dr. K. SACHS,* M.Sc., A.I.M. (Member): The appearance of striations in a configuration suggesting evaporation or deposition from the vapour phase is an extremely interesting observation. The smoothing of the striations by treatment in hydrogen or argon supports the authors' view that in each case the surface adopts the microgeometric profile corresponding to its state of minimum free energy. However, the detailed mechanism for these surface undulations put forward on p. 91 of the paper, that the migration of nickel atoms into sites vacated by oxidized chromium atoms causes a reorganization of the lattice which enables the surface to attain its equilibrium profile, encounters a number of grave difficulties. This mechanism would require nothing more than local diffusion, which presumably takes place at these temperatures even in the absence of selective oxidation. The mechanism must also account for the disappearance of the striations in pure hydrogen when chromium is reduced back and diffuses into the metal, or in argon, when the chromic oxide coalesces to leave a metallic surface and there is no change in the composition of the underlying metal at all. Moreover, the amount of material involved in the selective oxidation of an alloy containing 4.6% chromium is presumably very small compared with the material involved in the formation of striations; the authors themselves draw attention to the fact that Elam, Gwathmey and Benton, Jacquet, and Shuttlesworth, King, and Chalmers have observed analogous phenomena in pure copper and silver. It

seems reasonable to conclude, therefore, that the striations are formed by a mechanism involving a substantial amount of nickel.

A detailed mechanism for copper has been put forward by Erdmann-Jesnitzner and Günther.† I feel that a generally applicable explanation can be based on the following considerations.

In pure metals the striations are formed under conditions of atmosphere and temperature which prevent the formation of a stable oxide, and in the present case the oxidation of nickel is similarly suppressed. It must be borne in mind, however, that we are dealing with kinetic equilibria and that the absence of a stable oxide from the surface of the copper and silver specimens, or of nickel oxide from the chromic oxide layer (the amount of nickel in solution in the oxide could evidently not be determined), implies that the oxide dissociates as soon as it forms and not that it never forms at all. In this rapid alternation of formation and dissociation of oxide, metal atoms will enter the oxide preferentially from points of high surface energy and will be deposited at points of low surface energy, thus forming the equilibrium profile which, as the authors observe, may be flat or striated, depending on experimental conditions. Growth of idiomorphic crystals is generally observed from solution or from a vapour phase; it is suggested that in the present case the metastable oxide plays an analogous role.

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† F. Erdmann-Jesnitzner and F. Günther, *Z. Metallkunde*, 1954, 45, 407.

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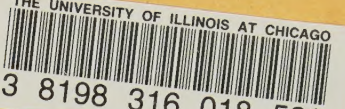
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